TOXIC HOTSPOTS:

A Greenpeace Investigation of GUJARAT INDUSTRIAL ESTATES

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Organic and heavy metal contaminants in samples taken at three industrial estates in Gujarat, India

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Authors:
Labunska, I., Stephenson, A., Brigden, K., Stringer, R., Santillo, D. Johnston, P.A. & Ashton, J.M.

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Greenpeace Research Laboratories, Department of Biological Sciences,
University of Exeter, Exeter UK
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Address:
Greenpeace Research Laboratories, Department of Biological Sciences,
University of Exeter EX4 4PS, UK

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Executive summary

Following a sampling and analysis programme carried out in 1996, in May 1999, Greenpeace International carried out a further programme at industrial estates located at Ankleshwar, Nandesari and Vapi in Gujarat, India. These estates consist of an estimated 3,000, 300 and nearly 2,000 industrial units respectively. The industries utilise common effluent treatment plants (CETPs) to varying degrees to treat process waste streams. Considered individually (and in aggregate) the diverse chemical manufacturing processes involved generate highly complex waste streams for which techniques to deal with them either do not exist or are unproven in practical application (Englande 1994). Common effluent treatment plants have been promoted in the region as a long-term solution to the environmental problems arising from contaminated wastewater disposal. This report utilises data from samples taken from the open waste-water channels and common effluent treatment plants (CETPs) associated with these industrial estates and from the surrounding environment to demonstrate that in a large majority of cases, such plants do not adequately treat industrial effluents generated by these industries. Accordingly, environmentally significant chemical contaminants, rather than being treated and degraded are still being discharged to the wider environment.

Comparison of sample results obtained in 1996 with those obtained from the current programme in 1999 revealed that similar profiles of persistent organic pollutants and heavy metals to be present in samples. The CETPs were brought on line subsequent to the 1996 programme and presumably were intended to address the diverse chemical mixtures being discharged. This strategy has demonstrably failed. In one instance wider range of organic contaminants was found and included, specifically, brominated compounds and the insecticide chlorpyrifos. In both 1996 and 1999 the Greenpeace International programmatic studies in the vicinity of the Ankleshwar estate demonstrated the widespread occurrence of *inter alia* chlorinated benzenes, chlorinated benzenamines, certain polychlorinated biphenyls, chlorinated toluenes and brominated organic compounds. Moreover, the widespread contamination of the Ankleshwar area with elevated levels of copper is indicative of the generally inadequate process control and waste management practices employed on this estate.

Common Effluent Treatment Plants are known to concentrate heavy metal contamination in solid residues, which far from providing a solution, is merely the transfer of contamination from one environmental medium to another and is associated with specific waste disposal problems. Notwithstanding this cadmium levels in the effluent from the CETP on the Vapi industrial estate clearly demonstrate that not all the heavy metals are removed from the liquid phase, resulting in significant, direct, discharges to aquatic systems outside the plant. Further confirmation of the relative inefficiency of CETPS in degrading chemicals present in the influent stream is provided by sludge/sediment samples taken at Ankleshwar. In this case, samples of sludge collected adjacent to the final settling lagoon of the CETP on Ankleshwar were found to contain the same organic contaminants as sediment samples taken from the Amlakhadi channel into which this plant discharges. The influence of historical discharges may be largely discounted. The presence of chlorinated and brominated benzamines, which are generally accepted as having a short environemental half-life indicates that recent discharges to the channel are responsible for this contamination.

The widespread impact of poor management and control practices is illustrated by

groundwater samples taken in the vicinity of Sarigam. This is located a few kilometres south of the Vapi industrial estate. Upon analysis, this groundwater was found to contain trichloroethene, benzene, chlorobenzene, 1,3- and 1,4-dichlorobenzenes. The concentration of trichloroethene present exceeded the US EPA permissible levels set for drinking water by a factor of four. Benzene is a known human carcinogen and dichlorobenzene is a persistent organic contaminant that is itself resistant to microbial breakdown and is suspected to inhibit the microbial degradation of other chemicals.

This report highlights the complexity of the chemical mixtures that continue to be discharged and to persist in the environment in the Gujarat region. In this context it also discusses the limited utility and effectiveness of current treatment plants and outlines the need for an overall waste treatment strategy with a long-term goal of elimination of priority pollutants at source.

Introduction

The "Golden Corridor" of the Indian State of Gujarat is an industrial belt that runs along the main north-south highway, linking the southern town of Vapi, with northern State capital of Ahmedabad. It is so called because of the wealth that has been generated by rapid industrial development. However the price of this economic success has been, and continues to be, widespread and in many regions, severe environmental damage. This area includes the large industrial estates in Ankleshwar, Nandesari and Vapi (see Figure 1).

These industrial areas contain thousands of individual industrial units, including dye factories, textile, rubber, pesticide and paint manufacturers, pulp and paper producers, pharmaceutical, engineering and chemical companies (CPCB 1996, Bruno 1995, Nagar 1995). Visual surveys of the sites reveal industrial development that is haphazardly organised and poorly controlled, with facilities for waste management generally inadequate, and in many cases, non-existent. Widespread contamination of the industrial sites and surrounding areas is clearly observed. Poor health and safety, and waste management practices may pose serious health hazards, not only to the workers, but also to the communities within and around the sites, and the villages downstream from the effluent discharges.

In all three industrial estates, piles of sludge and solid waste are dumped indiscriminately on open ground, and open roadside ditches are used to carry mixed effluent to pumping stations and rivers. Where waste treatment facilities do exist (often in the form of common effluent treatment plants, CETPs), only a limited range of physical, biological and simple chemical variables are addressed (e.g. pH, conductivity, dissolved and suspended solids, BOD, COD, nitrogen and phosphorus, along with certain other major ions). This is a common feature of CETPs (Hadjivassilis *et al.* 1994), since treatment facilities are fundamentally unable to deal adequately with persistent organic compounds and heavy metals. Indeed, their operation may well be severely hindered by the presence of such contaminants, which can exert toxic effects on the micro-organisms responsible for biological waste treatment.

At best, therefore, CETPs serve to concentrate persistent pollutants from liquid waste streams into highly contaminated sludges. Far from solving a problem, this simply creates another hazardous waste stream. In addition, by combining wastewaters from a large

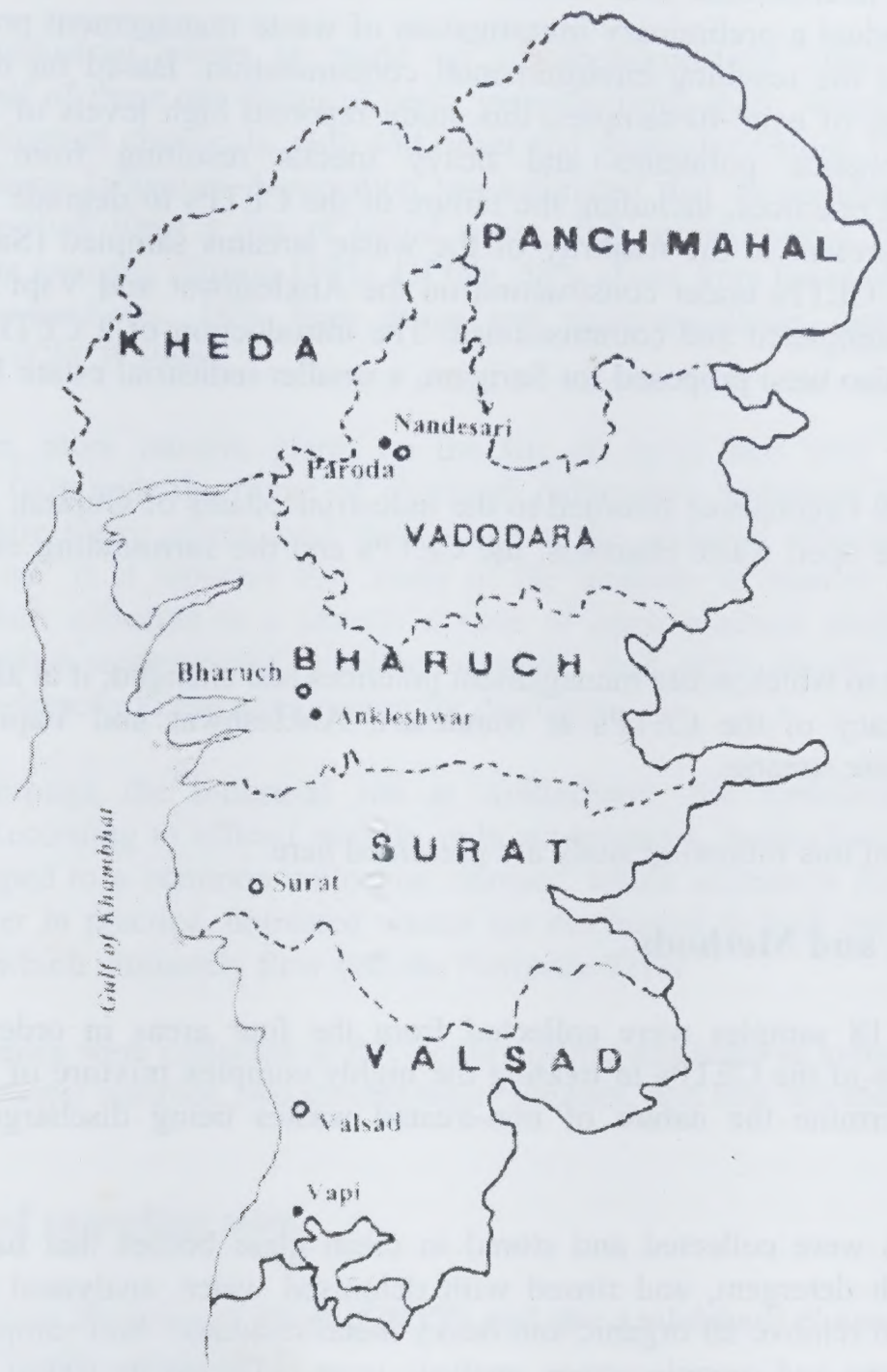

Fig. 1 Location of Ankleshwar, Nandesari and Vapi Industrial Estates, Gujarat, India

number of industrial units, often engaged in very different manufacturing processes, highly complex effluents and wastes, with wholly unpredictable toxicological properties may be generated. And as existing pollution-control legislation does not demand detailed chemical characterisation of effluents, many components of wastes are overlooked, including persistent organic compounds. Consequently wastewaters that meet these

limited legislative requirements are considered acceptable for discharge to surface water, despite the fact that high concentrations of toxic and persistent chemicals may still be present.

Greenpeace International first visited the industrial estates of Gujarat in April 1996 in order to conduct a preliminary investigation of waste management practice the chemical industry and the resulting environmental contamination. Based on the results obtained from analysis of over 40 samples, this study reported high levels of contamination with persistent organic pollutants and heavy metals resulting from inadequate waste management practices, including the failure of the CETPs to degrade the persistent toxic substances present in the majority of the waste streams sampled (Santillo *et al.* 1996). Since 1996, CETPs under construction on the Ankleshwar and Vapi estates at that time have been completed and commissioned. The introduction of a CETP to treat combined wastes has also been proposed for Sarigam, a smaller industrial estate 10 kilometres South of Vapi.

In May 1999 Greenpeace returned to the industrial estates of Gujarat, with the aim of re-sampling the open waste channels, the CETPs and the surrounding environs, in order to determine:-

a) the extent to which waste management practices had changed, if at all, since 1996 and;
b) the efficacy of the CETPs at Nandesari, Ankleshwar and Vapi in addressing the complex waste streams.

The results of this follow-up study are presented here.

Materials and Methods

A total of 18 samples were collected from the four areas in order to determine the effectiveness of the CETPs in treating the highly complex mixture of waste they receive, and to determine the nature of non-treated wastes being discharged into local river systems.

All samples were collected and stored in clean glass bottles that had been thoroughly washed with detergent, and rinsed with deionised water, analytical grade pentane and nitric acid to remove all organic and heavy metal residues. Soil samples for heavy metal determinations and organic screen analysis were collected in 100ml clear glass bottles, while aqueous samples were collected in 1-litre clear glass bottles. Aqueous samples for volatile organic compounds (VOCs) analysis were collected in 125ml amber glass bottles capped with a ground glass stopper. Bottles were filled completely, ensuring that no air bubbles were present. All samples were stored cold, kept cold during transit, and refrigerated at 4^0C immediately on arrival at the Greenpeace Research Laboratories.

Detailed descriptions of sample preparation and analytical procedures are presented in Appendix 1.

1. Ankleshwar Industrial Estate

1.1 Introduction

The Ankleshwar industrial estate is made up of approximately 3,000 individual companies. Over half of these are chemical units, manufacturing dyes, paints, fertilisers, pharmaceuticals, industrial chemicals, pulp and paper and pesticides (Bruno 1995, CPCB 1996). The Ankleshwar Industrial Association has estimated that its members generate between 250-270 million litres a day of liquid waste, and approximately 50 thousand tonnes of solid waste annually (Bruno 1995). Of this, 58% arises from the manufacture of dyes and dyes intermediates, 19% from drugs and pharmaceuticals, and 5% from inorganic chemicals (CPCB 1996).

Many of the larger, more modern plants on the site do have their own wastewater treatment facilities (although the range of chemical parameters addressed is likely to remain limited), while many others send their waste to the common effluent treatment plant described above. It is reported that many of the medium to smaller sized units simply discharge their effluents to a chaotic system of open roadside ditches and an incomplete and broken underground pipeline network, that carry mixed effluent to pumping stations or directly to the river system for discharge.

Two creeks run through the industrial site at Ankleshwar, the Amlakhadi and the Sarangpur Khadi. According to official records, only wastewaters, having being treated at the CETP, are pumped to a common collection channel, which ultimately flows into the Amlakhadi. However in practice, untreated wastes are discharged to both the Amlakhadi and the Sarangpur, which ultimately flow into the Narmada River.

A total of eight samples were collected in the vicinity of the Ankleshwar industrial estate, including two wastewater samples, two ground water samples, and four sediment samples.

1.2 Description of sampling sites

The Common Effluent Treatment Plant (CETP) and the Amlakhadi channel (IT9048, IT9049, IT9051 and IT9052)

The Common Effluent Treatment Plant (CETP) receives a complex mixture of wastes from a large number of sources on the industrial estate. While some waste is piped directly to the CETP for treatment, the majority is brought in by tanker. A sample of sludge (IT9048) was taken from a pile adjacent to the final settling lagoon of the CETP, from where treated wastewater is discharged into the Amlakhadi. This sludge is believed to be dredged from the final settling lagoon and local sources report that it may be taken to a cement kiln where it is burned as fuel.

A combined solid wastes dump has recently been introduced on the Ankleshwar industrial estate. It was not possible to gain access to this dump area, and there was no visible surface leachate from the dump at the time of sampling.

A matrix of wastewater pipes run throughout the Ankleshwar industrial estate, some of which are used to carry wastewater from a number of sources to the CETP. Some of these pipes, however, are used to discharge untreated wastewater to the Amlakhadi, from where it flows into the Narmada River.

A sample of effluent (IT9049) was taken from a half-full 25 centimeters diameter pipe which was discharging effluent into a channel that leads to the Amlakhadi. This wastewater was pungent, and extremely acidic. It was not possible to determine the source of this effluent. This sample was not intended to be representative of other wastes entering the Amlakhadi, but merely to demonstrate the potential for contamination of the aquatic environment resulting from such discharges.

The Amlakhadi was previously sampled in 1996, at a location near to the Kadakia College. The water was found to contain many organochlorine compounds, including trichlorotoluene and chlorinated benzenes, as part of a diverse mixture of organic pollutants. Sediment collected from the same location at that time had a very high organic content, and contained oils, organic sulfur compounds and organochlorines. Sediments collected from a number of locations along the Amlakhadi contained heavy metals above levels expected for river sediments, including mercury, chromium, cadmium and copper. During monsoon the Amlakhadi overflows, submerging the surrounding lands in polluted water (Santillo *et al.* 1996).

In order to determine the current levels of pollution in the Amlakhadi, the channel was resampled. A sample of river water (IT9051) and sediment (IT9052) were taken from the Amlakhadi at the Ambroli bridge, near to the Central Industries Security Force. This location is approximately 2.5 kilometres downstream of the Ankleshwar industrial estate, and 0.5-1 kilometres downstream of the confluence of the Amlakhadi and the Panoli channel. The river contained large amounts of silt at this point.

Sarangpur Channel (IT9043)

A sample of sediment (IT9043) was taken from the Sarangpur channel, approximately 0.5 kilometres from the Sarangpur village, and approximately 0.5 kilometres downstream from the industrial estate. At this point, a solid wastes dump lies adjacent to the Sarangpur channel. According to official sources, the dumping of solid industrial wastes in this area has now been discontinued. It has been reported by locals, however, that the dumping continues. There appeared to be no measures in place to prevent leaching from the solid wastes dump into the Sarangpur channel. At the point of sampling, the channel was approximately 5 centimetres deep and not flowing. The channel is dammed at this point, and the channel is a dry bed upstream of the dam.

Sarangpur Village (IT9044 and IT9046)

Two samples of ground water were taken from the village of Sarangpur, approximately 1 kilometre from the Ankleshwar estate. One sample (IT9044) was taken from an open well located approximately 200 metres from the Sarangpur channel, and approximately 0.5 kilometres from the point at which the Sarangpur channel was sampled (IT9043). The well was approximately 25 metres deep, and the ground water was red-brown in colour, foaming upon agitation. When used for irrigation, the water is reported, by a local farmer,

to cause crops of pigeon-peas to fail, and to give a poor yield of malformed fruit from aubergine plants. Prolonged contact of unprotected skin with this water is likewise reported to result in splitting of the skin. A local farmer reported that eleven other wells in Sarangpur village contained water that appears to be of a similar quality.

A further ground water sample (IT9046) was taken from an approximately 35 metre deep bole-hole located in the village of Sarangpur, on the border of Yogi Nagar and Bapu Nagar I settlements. Freshly drawn water from this bore-hole is initially clear and colourless, though exposure to sunlight results in a slight pink colouration after only 10 minutes. Locals reported that either boiling, or exposure to sunlight for a day, results in the water becoming dark red, with a scum on the surface. Use of the water for washing was likewise reported to cause skin irritation. It was reported by locals that this type of colouration of the water has been observed since 1985, though the length of time before a new bore starts to give contaminated water has decreased over the years. A new bore would previously have given uncontaminated water for up to 4-5 years, while at the present a new bore produces contaminated water almost immediately.

Heubach Colour Limited (sample IT9050)

Numerous unofficial dumps of unlabelled industrial wastes can be observed throughout the industrial estate. The waste is generally lying in uncovered piles, with no visible means to prevent leaching or spreading of the wastes. A notable example of this is a large amount of blue-green solid waste that has been dumped in an area of approximately 60 metres by 60 metres, on waste ground adjacent to the Heubach Colour Limited plant. A sample of which was collected for analysis.

Sample Number	Sample Description
IT9043	Sediment collected from the Sarangpur channel, prior to confluence with the Narmada River, approximately 0.5 kilometres from the Ankleshwar industrial site, and approximately 0.5 kilometres from the village of Sarangpur.
IT9044	Irrigation water from an open well in the village of Sarangpur, approximately 200 metres from the Sarangpur channel, and 1 kilometre from the Ankleshwar industrial site.
IT9046	Groundwater collected from a bore-hole in the village of Sarangpur, between the districts of Yogi Nagar and Bapu Nagar I. Used as drinking water.
IT9048	Sludge collected adjacent to the final settling lagoon of the Ankleshwar Common Effluent Treatment Plant.
IT9049	Untreated effluent collected from a pipe discharging into a channel that leads to the Amlakhadi channel.
IT9050	Blue / green solid waste collected from waste ground adjacent to Heubach Colour Limited, Ankleshwar.
IT9051	Water from the Amlakhadi channel at Ambroli bridge, approximately 2.5 kilometres downstream of the Ankleshwar industrial site, and 1 kilometre downstream of the Panoli confluence
IT9052	Sediment collected from the Amlakhadi channel (see IT9051)

Table 1.1 Descriptions of samples collected from Ankleshwar, Gujarat, India 1999.

1.3 Results and discussion

A total of eight samples were therefore collected from this industrial area (see Table 1.1 for full sample descriptions). Water samples IT9044 and IT9046 were analysed for volatile organic compounds only (see discussion below). The other six samples (IT9043, IT9048, IT9049, IT9050, IT9051 and IT9052) have been analysed for semi-volatile organic compounds and heavy metals. Details of the analytical methods used are given in Appendix 1.

The results of organoscreen analysis are presented in Table 1.2a. Groups of organic compounds reliably identified in these samples are presented in Table 1.2b. List of all reliably identified organic compounds and groups of tentatively identified compounds are presented in Appendix 2 (Tables 1.2c and 1.2d).

Most of the samples from this area contained wide range of organic contaminants with organohalogen compounds being the major contributor. Hexachlorobenzene, chlorinated benzenamines and several isomers of PCBs were identified in five samples, di- and trichlorobenzenes in four samples, and tetra- and pentachlorobenzenes and chlorinated toluenes in three samples. Brominated organic compounds were also identified in three samples (see Table 1.2a). Very similar contaminants, typical from mixed chlorine industries, were found in samples IT9048 and IT9049 as in IT9051 and IT9052.

Sample Code	Compounds isolated	Number Reliably identified (%)	Halogenated Compounds	PAHs	Phenolic compounds	Phthalates	Organosulphur compounds	Organonitrogen compounds	Organophosphorus compounds	Other aromatics	Aliphatics
IT9043	23	8(35%)	2	0	0	0	0	0	0	0	6
IT9048	164	74(45%)	28	7	0	0	7	2	0	4	23
IT9049	135	68(51%)	19	3	0	1	7	13	0	15	10
IT9050	74	28(38%)	9	1	1	3	0	1	0	7	5
IT9051	96	49(51%)	18	7	0	1	3	1	0	7	12
IT9052	170	55(34%)	20	0	4	0	1	1	3	4	23

Table 1.2a. Results of organoscreen analysis of sediment, solid waste, industrial waste water and river water samples collected in the vicinity of the Ankleshwar Industrial Estate, Gujarat, INDIA

Results of the heavy metals analysis are presented in Tables 1.3a (solid samples) and 1.3b (aqueous samples). The results show that high levels of copper were found in every sample. Levels in the solid samples ranged from 11.75 g/kg in sample IT9050, collected from a pile of blue / green waste close to the Huebach Colour Limited (dye manufacturers) plant, to 112.5 mg/kg found in the sediment of the Sarangpur. Aqueous samples also contained significant copper levels, with over 6 mg/l present in the unidentified effluent (IT9049), and nearly 600 ug/l present in the river water of the Amlakhadi (IT9051). Sample IT9051 also contained extremely high levels of manganese, and significant levels of cadmium, chromium, nickel and zinc. Sediment sample IT9052, also collected from the Amlakhadi channel, contained elevated levels of chromium, mercury and zinc.

Groups of compounds reliably identified	Number of samples	Sample Codes
ORGANOHALOGEN COMPOUNDS		
Dichlorobenzenes	4	IT9048, IT9049, IT9051, IT9052
Trichlorobenzenes	4	IT9048, IT9049, IT9051, IT9052
Tetrachlorobenzenes	3	IT9048, IT9051, IT9052
Pentachlorobenzene	3	IT9048, IT9049, IT9052
Hexachlorobenzene	5	IT9043, IT9048, IT9049, IT9050, IT9052
Chlorinated benzenamines	5	IT9048, IT9049, IT9050, IT9051, IT9052
Brominated benzenamines	2	IT9048, IT9051
Brominated benzenes	1	IT9048
Chlorinated toluenes	3	IT9048, IT9051, IT9052
Brominated toluenes	1	IT9048,
Chlorinated xylenes	1	IT9050
Brominated xylenes	1	IT9050
Brominated methoxybenzenes	1	IT9048
Polychlorinated benzonitriles	1	IT9050
Polychlorinated pyridine derivatives	2	IT9051, IT9052
Polychlorinated butadienes	1	IT9049
PCBs	5	IT9043, IT9048, IT9049, IT9051, IT9052
POLYCYCLIC AROMATIC HYDROCARBONS		
Naphthalene and its derivatives	3	IT9048, IT9049, IT9051
Phenanthrene and its derivatives	1	IT9050
PHENOLIC COMPOUNDS		
Octyl phenol	1	IT9050
Cresols	1	IT9052
Phenol	1	IT9052
Dichlorophenol	1	IT9052
PHTHALATES		
DEHP	3	IT9049, IT9050, IT9051
DiBP	1	IT9050
DBP	1	IT9050
OTHER AROMATICS		
Biphenyl and its derivatives	4	IT9048, IT9049, IT9050, IT9051
Alkylated benzene derivatives	5	IT9048, IT9049, IT9050, IT9051, IT9052
Dibenzothiophene and its derivatives	2	IT9048, IT9051
Other organosulphur compounds	4	IT9048, IT9049, IT9051, IT9052
Benzenamine and its derivatives	2	IT9049, IT9052
Azobenzene derivatives	3	IT9048, IT9049, IT9051
Other organonitrogen compounds	1	IT9049
Organophosphorus compounds	1	IT9052
Benzyl benzoate	1	IT9052
ALIPHATICS		
Linear alkanes and alkenes	6	IT9043, IT9048, IT9049, IT9050 IT9051,IT9052
Cyclic alkanes and alkenes	2	IT9043, IT9052

Table 1.2b. Groups of organic compounds reliably identified in sediment, solid waste, industrial wastewater and river water samples collected in the vicinity of the Ankleshwar Industrial Estate, Gujarat, INDIA

Background information on the metals and organic compounds found in these samples, including common sources, environmental behaviour and toxicological properties, are presented in the Appendix 3 and Appendix 4 at the end of this report. Possible sources of these metals and organic compounds in these samples are discussed below.

Sample Number	Cd (mg/kg)	Cr (mg/kg)	Co (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
IT9043	n/d	69.1	25.0	112.5	2.2	1009.6	1.4	50.7	62.5
IT9048	n/d	12.0	9.0	2933.0	17.0	104.0	1.2	18.0	83.0
IT9050	n/d	33.0	n/d	11750.0	29.0	98.0	0.2	23.0	147.0
IT9052	1.9	137.7	6.6	1434.9	67.0	219.8	3.7	30.2	159.4

Table 1.3a Results of heavy metals analysis (expressed as mg/kg dry weight), Ankleshwar, Gujarat, India 1999

Sample Number	Cd (ug/l)	Cr (ug/l)	Co (ug/l)	Cu (ug/l)	Pb (ug/l)	Mn (ug/l)	Hg (ug/l)	Ni (ug/l)	Zn (ug/l)
IT9049	<10	540	<10	6360	140	420	<2	100	160
IT9051	20	90	<10	580	<30	15610	<2	270	280

Table 1.3b Results of heavy metals analysis (expressed as ug/l), Ankleshwar, Gujarat, India 1999

The common effluent treatment plant (CETP) and the Amlakhadi channel (IT9048, IT9049, IT9051 and IT9052)

Four samples were taken in and around this area.

Sludge sample IT9048 was collected adjacent to the CETP lagoon. 164 organic compounds were isolated from this sample. 74 compounds (45%) were reliably identified, 28 of those being organohalogen compounds including di-, tri-, tetra-, penta- and hexachlorobenzenes, tribromobenzene, chlorinated and brominated benzenamines, chlorinated and brominated toluenes, and two PCBs (PCB-135 and PCB-136). Other aromatic compounds found in this sample included naphthalene derivatives, biphenyl and its derivatives, alkylbenzenes, organosulphur and organonitrogen compounds, and linear alkanes and alkenes.

This sample contained high levels of copper, therefore illustrating that even if the CETPs are capable of removing heavy metals from the in-coming waste stream, metals are still left in concentrated solid residues. Possible sources of copper are numerous, as the metal and its compounds are extensively used as alloys and electrical conductors, dyes, printing inks, catalysts, pesticides, disinfectants and fertilisers (ATSDR 1997). Production and use of any of these could release high levels of copper into the environment, and as effluent streams are mixed in the CETP and the open ditches, it is impossible to trace individual waste streams and sources.

Effluent sample IT9049 was collected from an unidentified pipe discharging directly to the Amlakhadi. 135 organic compounds were isolated from this sample. 68 compounds (51%) were reliably identified. Among those, 19 compounds were organohalogens including di-, tri-, penta- and hexachlorobenzenes, chlorinated benzenamines, tetra- and penta-butadiene, and five PCBs (PCB-3, PCB-10, PCB-13, PCB-19 and PCB-24). Other organic compounds found in this samples were naphthalene and its derivatives, one phthalate ester (DEHP), biphenyl and its derivatives, alkylbenzenes, organosulphur compounds, benzenamine and several alkylated benzenamines, aliphatic hydrocarbons, and several

organonitrogen compounds including benzonitrile, nitrobenzene, carbazole, phenazine and a pyridine derivative.

This sample also contained high levels of copper, along with significant levels of chromium. Chromium and its compounds are used in alloys, tanning agents, textile pigments and preservatives, pesticides, catalysts and corrosion inhibitors (ATSDR 1997). Again due to the industrial diversity of the estate and the mixing of waste streams prior to discharge, individual sources of chromium cannot be traced.

Two samples (water sample IT9051 and sediment sample IT9052) were collected from the Amlakhadi channel. 96 and 170 organic compounds were isolated from the samples IT9051 and IT9052 respectively. 49 compounds (51%) and 55 compounds (34%) were reliably identified. Both water and sediment samples contained wide range of compounds similar to those isolated from the CETP-related samples including chlorinated benzenes, chlorinated benzenamines, chlorinated toluenes, chlorinated pyridines, alkylbenzenes, PCBs, organosulphur compounds and linear aliphatics. Only sample IT9051 contained brominated benzenamines, naphthalene and its derivatives, biphenyl and its derivatives, DEHP, dibenzothiphenes, and azobenzene derivatives. At the same time, sample IT9052 also contained penta- and hexachlorobenzenes, which were not present in the sample IT9051, as well as phenolic compounds (phenol, cresols and dichlorophenol), alkylated benzenamine, benzyl benzoate, and organophosphorus compounds including insecticide chlorpyrifos and two relative compounds.

All four samples (IT9048, IT9049, IT9051 and IT9052) indicate contamination of this site by a wide range of organic compounds, the majority of which are toxic to both the environment and humans, and may persist for a long time. In the previous study conducted by Greenpeace (Santillo *et al.* 1996), water and sediment samples from the Amlakhadi channel showed very similar patterns of organic contaminants to the current study. Additionally, however in the current study a wider range of organic contaminants was found, including brominated compounds and the insecticide chlorpyrifos.

It is clear that the operation of the CETP is not effective because the same organic compounds were found in both sediment sample from CETP lagoon (sample IT9048) and in sediment and water from Amlakhadi channel which supposedly receives treated wastes (samples IT9052 and IT9051 respectively). Additionally, toxic chemicals are undoubtedly entering the Amlakhadi channel from the pipes carrying untreated wastewater. Some of the organic compounds found in the Amlakhadi channel samples may represent past contamination because they are persistent (for example, chlorinated benzenes). However, the presence of other halogenated compounds, such as chlorinated and brominated benzenamines, is a sign of current input, because these compounds are likely to break down more rapidly when released to the environment (Kosson & Byrne 1995). More information on toxicological profiles, uses, production and environmental behaviour of key organic compounds identified in these samples is presented in Appendix 3.

Water sample IT9051 contained high levels of cadmium, chromium, copper, manganese, nickel and zinc. Whilst sediment sample IT9052, collected from the same sampling point, contained high levels of copper, and elevated levels of chromium, mercury and zinc. Possible sources of copper and chromium are described above. Possible sources of the other metals include the following (ATSDR 1997):

Cadmium and its compounds are used in metal plating, nickel-cadmium batteries, pigments and PVC stabilisers. Nickel and its compounds are used in alloys, batteries, and catalysts. Mercury and its compounds are used in batteries, catalysts, thermometers, pharmaceuticals, pesticides and in the manufacture of chlorine. Zinc and its compounds are used as alloys, pesticides, catalysts, PVC stabilisers, fertilisers, paints, pigments and dyes. Manganese and its compounds are used in alloys, batteries, catalysts, fertilisers, pesticides and disinfectants.

Levels of these metals found naturally in unpolluted freshwater ecosystems are low. For example, river water levels of cadmium and chromium are usually less than 1 ug/l (ATSDR 1997, WHO 1992), yet 20 ug/l of cadmium and 90 ug/l of chromium were detected in sample IT9051. Similarly river water levels of copper, manganese, nickel and zinc usually range from 20-50 ug/l (ATSDR 1997). Therefore, depending on the reference value used, copper levels in IT9051 exceeded background concentrations by approximately 12-30 times, manganese by 310-780 times, nickel by 5-13 times and zinc by 5-14 times.

Levels of mercury in uncontaminated sediments are extremely low, with usual concentrations ranging from 0.2-0.35 mg/kg (Salomons and Forstner 1984). Therefore in sample IT9052, levels approximately 10-18 times background concentrations are present. Background levels of copper, zinc and chromium are usually less than 100 mg/kg, and again these levels are exceeded in sample IT9052.

The environmental behaviour and toxicological properties of these metals are discussed in the Appendix 4 at the end of this report.

Sarangpur channel (IT9043)

One sample of sediment was collected from the Sarangpur channel. 23 organic compounds were isolated from this sample. 35% of those were reliably identified, with linear and cyclic aliphatic hydrocarbons being dominant. Additionally, two organochlorine compounds, hexachlorobenzene and one isomer of PCBs (PCB-9) were also reliably identified in this sample.

Hexachlorobenzene strongly adsorbs to soil particles (Bahnick & Doucette 1988). If discharged into water, it can be transported for long distances attached to the particles and finally deposit. It may persist in the soil, air, surface and ground water for many years (Howard 1991). It is known that hexachlorobenzene is commonly used as an intermediate in organic syntheses (Budavari et al. 1989) and may be formed as an unwanted by-product in the synthesis of other organochlorine compounds (Newhook & Meek 1994, Sala et al. 1999). Thus, the presence of hexachlorobenzene in this sediment sample may be associated with wastes generated from Ankleshwar Industrial Estate, which includes such industries.

PCB-9, or 2,5-dichlobiphenyl, is a representative of a large group of polychlorinated biphenyls. The PCBs have been used widely in different applications, including transformer oils, hydraulic fluids, plasticisers, 'kiss-proof' lipsticks and carbonless copy papers. They were also used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 1997). PCBs were always marketed as technical mixes rather than individual chemicals (de Voogt & Brinkman 1989).

Additionally, PCBs used in transformer oils were usually mixed with chlorobenzenes (mainly trichlorobenzenes and tetrachlorobenzenes) as solvents (Swami *et al.* 1992, de Voogt & Brinkman 1989). Tri- and tetrachlorobenzenes were not found in this sample. Therefore the presence of PCB-9 in this sample may be associated with an alternative source. For example, it may have been formed as a by-product of the chlorine chemical industry. Such industries include the PVC industry. Waste EDC tars, together with aqueous effluents, are known to be contaminated by dichlorobiphenyls (see: US EPA 1994).

Levels of heavy metals in this sediment sample were significantly lower than those found in a similar sample collected from the Amlakhadi channel. However the level of copper found was higher than that usually associated with uncontaminated sediments. Background levels of copper are usually quoted as less than 50 mg/kg (Salomons and Forstner 1984), twice this concentration was detected in sample IT9043.

It is clear, based on our other results (from both 1996 and 1999), and our knowledge of the types of industries located in Ankleshwar, that copper contamination in this area is widespread. Such generally elevated levels of copper are again indicative of the inadequate process control and waste management practices employed by many industries of the Ankleshwar estate.

Sarangpur Village (IT9044 and IT9046)

Only one volatile organic compound, 1,2,4-trichlorobenzene, was found in the sample IT9044 at a concentration of 15ug/l. Environmental releases of this compound may result from industrial discharges and from spillage of dielectric fluids. 1,2,4-trichlorobenzene may be found in all environmental media. In groundwater, it may persist for several years (Howard 1991). Trichlorobenzenes have also been found in drinking water, but rarely above 1ug/l (WHO 1993). This compound may be used as a solvent and an intermediate in organic synthesis (Giddings *et al.* 1994). Additionally, 1,2,4-trichlorobenzene may be formed through the dehydrohalogenation of the unwanted isomers of the production of the pesticide 1,2,3,4,5,6-hexachlorocyclohexane (HCH).

No volatile organic compounds were found in the drinking water sample IT9046. It was not possible to determine the agents responsible for the colour change reported upon exposure to sunlight or heat.

Heubach Colour Limited (sample IT9050)

One sample of blue-green waste was collected close to this dye and pigment factory. The intense colour was due to the presence of high levels of copper, which is widely used in the manufacture of dyes, pigments and printing inks (ATSDR 1997). The lack of any suitable containment facility for this waste is a concern, and may be one of the reasons why copper contamination in and around this industrial estate is so widespread. The environmental behaviour of copper and its toxicological properties are given in an appendix at the end of this report.

74 organic compounds were isolated from this sample. 28 compounds (38%) were reliably identified, including nine halogenated compounds (hexachlorobenzene, tetra- and

pentachlorinated benzenamines, chlorinated and brominated xylenes, and pentachlorobenzonitrile), three phthalate esters (DEHP, DBP and DiBP), octyl phenol, alkylated biphenyl and benzene derivatives, linear aliphatic hydrocarbons, and phenanthrene and its derivatives. The majority of these compounds is toxic and persistent and their appearance in the sample may be associated with dye and pigment manufacture. More information on toxicological profiles, uses, production and environmental behaviour of key organic compounds is presented in Appendix 3.

2. Nandesari Industrial Estate

2.1 Introduction

The Nandesari industrial estate was established in 1969, and is now made up of approximately 300 industrial units, including those that produce a wide range of chemicals, pharmaceuticals, dyes, pesticides and plastics (Tiwari and Mahapatra 1999, CPCB 1996). The main contributors to the total quantity of waste generated by the estate include dyes and dye intermediates manufacture (82%), and the production of drugs and pharmaceuticals (13%) (CPCB 1996).

Only 80 of the companies on site are known to send their effluents to the CETP (Tiwari and Mahapatra 1999), with plant operators unsure of what happens to the rest. However, as was seen in Ankleshwar, albeit on a much wider scale, indiscriminate dumping and the use of roadside ditches to carry waste are widespread and common practices.

From the CETP, effluents are carried along a communal channel (Bruno 1995). Known as the "Effluent Channel Project, this runs for 55 kilometres before discharging into the Mahi River estuary close to the point where it debouches to the Gulf of Khambat. It is likely, however, that additional untreated wastes from the site and from the surrounding area are also carried along this channel to the estuary.

A total of four samples were taken from the vicinity of the Nandesari industrial estate, including two wastewater samples, and two sediment samples.

2.2 Description of sampling site

The common effluent treatment plant (CETP) (IT9054)

The Common Effluent Treatment Plant (CETP) receives a complex mixture of wastes from a large number of different sources on the Nandesari industrial estate. A sample of sludge (IT9054) was taken from the final settling lagoon of the CETP, from which wastewater is discharged to the Mahi River estuary on the Gulf of Khambhat via the communal effluent channel.

In 1996, sludge from one of the CETP evaporation ponds was collected for analysis. This sludge was found to contain chlorinated toluenes and chlorinated naphthalenes (*Santillo* et al. 1996), none of which are efficiently degraded in standard effluent treatment plants. It is not clear whether sample IT9054 was from the same lagoon as that sampled on the previous occasion.

Communal Effluent Channel (The Effluent Channel Project) (IT9053, IT9055, IT9056)

Wastewaters from the CETP and from other sources are carried along a 55 kilometre long, partially covered, brick lined channel to the Mahi River Estuary close to the point where the estuary enters the Gulf of Khambhat. The discharge point is known as "Point J" and is located near to Sarod, north of Jambusar. The channel is approximately 4 metres deep, and carries wastewater to a depth of approximately 3 metres. The channel does not appear to be lined to prevent leaching of the wastewater to the surrounding land and groundwater. Along the length of the channel, small pumps can be observed removing wastewater for the irrigation of cultivated land. It has been reported, by locals, that some industries discharge untreated wastewater directly into the effluent channel at various points and that clean water is often added to the channel in order to dilute any pollutants in the wastewater.

A sample of treated wastewater (IT9053) was taken from the effluent channel at a point approximately 1 kilometre downstream of the CETP. Wastewater from other sources may discharge into the effluent channel prior to this point. It was not possible to access the effluent channel any closer to the CETP.

A further sample of wastewater (IT9056) was taken from the effluent channle approximately 2-3 kilometres downstream of the Nandesari estate, close to Koyli Point. This sample was taken to determine the nature of any additional pollutants resulting from the discharge of effluents (likely to be untreated) into the waste channel.

Located approximately 2 kilometres downstream of the Nandesari estate is an "escape" channel, to enable excess wastewater to overflow from the effluent channel into the Mini River which is a tributary to the Mahi River. It was reported by a local person that this escape channel flows for at least three months of the year.

There are a number of other chemical manufacturing plants close to the effluent channel between the Nandesari estate and the discharge point, Point J. Some of these are located close to Luna village, approximately 15-20 kilometres downstream of the Nandesari complex. It has been reported , by local people, that a number of these facilities discharge untreated or partially treated wastewaters into the effluent channel.

It was not possible to sample the wastewater from the effluent channel at the point of discharge, Point J. Three holding lagoons for wastewater from the effluent channel are located approximately 1 kilometre upstream of Point J. These lagoons are separately connected to the effluent channel via a sluice gate. All wastewater from the effluent channel flows through these holding lagoons to the discharge point, Point J. A sample of sediment (IT9055) from one of these lagoons was collected in order to give an indication of pollutants present in the wastewater flowing through the effluent channel on the basis that sediments tend to "integrate" contaminants present in the overlying water by adsorption processes.

Sample Number	Sample Descriptions
IT9054	Sludge collected from the CETP final settling lagoon.
IT9053	Treated effluent collected from the effluent channel between the CETP and the Gulf of Khambhat, approximately 1 kilometre downstream of the CETP.
IT9056	Effluent collected from the effluent channel approximately 2-3 kilometres downstream of the Nandesari estate.
IT9055	Sludge collected from one of three holding lagoons adjoined to the effluent channel, close to the point of discharge into the Gulf of Khambhat.

Table 2.1 Description of samples collected from Nandesari, Gujarat, India 1999.

2.3 Results and discussion

Four samples were collected from the Nandesari industrial area (see Table 2.1 for full sample descriptions).

Results of the organic screening analysis are presented in Tables 2.2a and 2.2b. A list of all reliably identified organic compounds and groups of tentatively identified compounds is presented in Appendix 2 (Table 2.2c).

Groups of compounds reliably identified	Number of samples	Sample Codes
ORGANOHALOGEN COMPOUNDS		
Dichlorobenzenes	4	IT9053, IT9054, IT9055, IT9056
Trichlorobenzenes	2	IT9054, IT9055
Tetrachlorobenzenes	1	IT9054
Pentachlorobenzene	1	IT9054
Hexachlorobenzene	1	IT9054
Chlorinated benzenamines	1	IT9054
Chlorinated toluenes	1	IT9054
Chlorinated naphthalenes	1	IT9054
Polychlorinated butadienes	1	IT9054
POLYCYCLIC AROMATIC HYDROCARBONS		
Naphthalene and its derivatives	2	IT9053, IT9054
9H-Fluorene	1	IT9056
Phenanthrene and its derivatives	2	IT9054, IT9056
PHENOLIC COMPOUNDS		
Alkyl phenol derivatives	2	IT9053, IT9056
OTHER AROMATICS		
Biphenyl and its derivatives	1	IT9056
Alkylated benzene derivatives	2	IT9053, IT9056
Organosulphur compounds	1	IT9054
ALIPHATICS		
Linear alkanes and alkenes	3	IT9054, IT9055, IT9056

Table 2.2a. Groups of organic compounds reliably identified in industrial wastewater and solid waste samples collected in the vicinity of the Nandesari Industrial estate, Baroda, Gujarat, INDIA

Sample Code	Compounds isolated	Number reliably identified (%)	Halogenated Compounds	PAHs	Phenolic compounds	Other aromatics	Aliphatics
IT9053	43	14(33%)	1	1	1	11	0
IT9054	169	49(27%)	15	12	0	2	19
IT9055	34	6(18%)	3	0	0	0	3
IT9056	65	20(31%)	3	7	1	4	5

Table 2.2b . Results of organoscreen analysis solid waste and industrial wastewater samples collected in the vicinity of the Nandesari Industrial estate, Baroda, Gujarat, INDIA

Results of the heavy metals analysis are presented in Tables 2.3a (solid samples) and 2.3b (aqueous samples).

Sample Number	Cd (mg/kg)	Cr (mg/kg)	Co (mg/kg)	Cu (kg/mg)	Pb (mg/kg)	Mn (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
IT9054	n/d	77.5	59.8	536.3	122.6	191.2	2.3	295.1	2762.6
IT9055	2.9	65.7	54.9	99.0	4.9	435.3	1.5	67.7	658.8

Table 2.3a Results of heavy metal analysis (expressed as mg/kg dry weight) Nandesari, Gujarat, India 1999

Sample Number	Cd (ug/l)	Cr (ug/l)	Co (ug/l)	Cu (ug/l)	Pb (ug/l)	Mn (ug/l)	Hg (ug/l)	Ni (ug/l)	Zn (ug/l)
IT9053	<10	<10	<10	10	40	40	<2	60	50
IT9056	<10	60	20	40	<30	90	<2	40	200

Table 2.3b Results of heavy metal analysis (expressed as ug/l) Nandesari, Gujarat, India 1999

The common effluent treatment plant (CETP) (IT9054)

169 organic compounds were isolated from the sediment sample collected from the CETP final settling lagoon (IT9054). 49 compounds were reliably identified including 15 organochlorine compounds: di-, tri-, tetra-, penta-, and hexachlorobenzene, chlorinated benzeneamines, chlorinated toluenes, chlorinated naphthalenes and tetra-, penta- and hexachlorobutadiene.

More information on toxicity, uses, production and environmental behaviour of key organic compounds is presented in Appendix 3.

Heavy metal analysis results show that significant levels of copper, lead, mercury, nickel, and zinc were found in the sludge collected from the CETP settling lagoon (IT9054). This illustrates, once again, that the CETP is only capable of redistributing heavy metal contaminants from the liquid to the solid sludge phase. While this may reduce the immediate loading to surface waters, it also creates an additional contaminated waste stream that must be addressed.

Possible sources of heavy metals are numerous and have been, with the exception of lead, described above. Lead is widely used in alloys, solder and batteries. Lead compounds have been used in paint pigments, PVC stabilisers, in pesticides, varnishes, lubricants, glazes and petrol additives (ATSDR 1997). Due to the diversity of the industries operating on the Nandesari estate, it is not possible to reconcile sources of lead any more specifically.

Communal Effluent Channel (The Effluent Channel Project) (IT9053, IT9055, IT9056)

43 organic compounds were isolated from the water sample IT9053 collected from the effluent channel approximately 1 kilometre downstream of the CETP. 14 compounds (33%) were reliably identified with alkylated benzenes being the major contributor. 1,4-dichlorobenzene, naphthalene and butylated hydroxytoluene (BHT) were also found in this sample.

As noted above, both the CETP and this channel receive the combined wastes from a variety of industries. Hence, the composition of the wastewater discharging into this channel may vary on a daily basis or even change several times per day depending upon which industries are contributing qualitatively and quantitatively to the overall effluent flow at any given time. This situation may be further exacerbated by the operation of many of the small to medium-sized plants largely in a batch, rather than continuous, mode of production. The compounds associated with crude oil or petroleum products were predominant in the water sample IT9053 at the time of sampling. The wide range of persistent organochlorine compounds in the sediment sample from the CETP final settling lagoon (IT9054) indicate, however, that these compounds have been discharged to the CETP at other times.

65 organic compounds were isolated from the water sample collected from the channel approximately 2-3 kilometres downstream of the Nandesari estate (IT9056). 20 compounds (31%) were reliably identified. These consisted of three isomers of dichlorobenzene, seven polycyclic aromatic hydrocarbons (PAHs), three alkylbenzenes, biphenyl, butylated hydroxytoluene and aliphatic hydrocarbons. Organic compounds found in this sample were similar to those found in the water sample IT9053 collected near to the CETP. The major difference evident was that two more dichlorobenzenes and additionally PAHs were identified in the sample IT9056 in comparison to sample IT9053. As noted previously, chlorinated benzenes are persistent compounds, which can be expected to be detectable at considerable distances from the initial point of discharge.

In the sediment sample IT9055, which was collected from one of the holding lagoons prior to discharge at Point J, only 6 compounds (18%) could be identified with high degree of reliability. Once again di- and trichlorobenzenes and aliphatic hydrocarbons predominated.

In general, analysis of the samples collected from this area showed that majority of organochlorine compounds were retained in the settling lagoon of the CETP (sample IT9054). Nevertheless, chlorinated benzenes were still found along whole length of the channel. As noted in the description of the Nandesari sampling program, water from the channel is used for irrigation. 1,4-Dichlorobenzene has been shown to inhibit the growth of cultured plant cells (Wang *et al.* 1996). These chemicals have been found in food, breast milk and drinking water in other industrialised countries (Meek et al. 1994). Moreover, they are also toxic to higher plants, inducing abnormal mitosis (cell division) in

onions for example (Ware 1988). More information on toxicity, uses, production and environmental behaviour of these and other key organic compounds is presented in Appendix 3.

Elevated levels of metals were not detected in the wastewater sample collected from the effluent channel approximately 1 kilometre downstream of the CETP (IT9053). The wastewater sample (IT9056) collected from approximately 2-3 kilometres downstream of the Nandesari estate, however, contained a number of metals including chromium, manganese and zinc. These were elevated above the levels found in sample IT9053.

For a number of metals, including chromium and mercury, levels found in the sludge collected from the effluent channel holding lagoons (IT 9055) were comparable with those found in the sludge collected from the CETP settling lagoon (IT9054). In addition, the concentration of manganese in the holding lagoon was higher than that found in the CETP sludge (IT9054). Although cadmium was not detected in the CETP sludge (IT9054), elevated levels were detected in the sludge from the holding lagoon (IT9055). These results are indicative of the discharge of wastewaters containing heavy metals to the effluent channel from sources other than the CETP.

3. Vapi Industial Estate

3.1 Introduction

The Vapi industrial estate is made up of nearly 2000 industrial units, that produce a wide range of chemicals, pharmaceuticals, dyes, pesticides and other agrochemicals, and plastics (Tiwari and Mahapatra 1999, CPCB 1996), with dye manufacturers and dye intermediate units contributing the largest quantity of hazardous waste (CPCB 1996). The situation regarding effluent treatment is same as that seen in Ankleshwar and Nandesari. Some companies send their waste to the common effluent treatment plant (CETP), whilst others dump solids indiscriminately and discharge their effluents into open ditches and lagoons.

The CETP has been completed and commissioned since the last study conducted by Greenpeace in 1996. Effluents from the CETP are discharged into the Damanganga River. However visual surveys of the plant reveal that some wastes are also discharged into this river, carried by a channel which appears to bypass the CETP.

A total of three samples were taken from the Vapi industrial estate, including two water samples, and one sediment sample.

3.2 Description of sampling sites

The Common Effluent Treatment Plant

In 1996, prior to the introduction of the Common Effluent Treatment Plant (CETP), samples of sludge collected from a common effluent channel at it's confluence with the Damanganga River contained, among other compounds, chlorinated benzenes and dichlorodiazobenzenes. Both the effluent and sediment samples collected from this channel also contained elevated levels of metals, including lead and mercury (Santillo *et*

al. 1996).

The now operational CETP receives a complex mixture of wastes from a large number of different sources. Treated wastewater is discharged into the Damanganga River, close to the CETP. In order to determine the effectiveness of the CETP in treating the complex mixture of wastes it receives, the discharge wastewater was of the CETP was sampled from the outfall pipe, on the bank of the Damanganga River (IT9058).

Adjacent to the outfall pipe of the CETP, a black stream of what appeared to be industrial wastewater flows from the direction of the CETP directly into the Damanganga River. This wastewater, although distinct from the CETP discharge, appeared to originate from the location of the CETP. A sample of the liquid from this flow (IT9059) and sediment from beneath the liquid (IT9060) were taken for analysis.

Sample Number	Sample Description
IT9058	Treated effluent collected from the Common Effluent Treatment Plant outfall pipe, at the point of discharge to the Damanganga River.
IT9059	Effluent collected from a black stream of industrial wastewater flowing into the Damanganga adjacent to the CETP outfall pipe.
IT9060	Sediment collected from a black stream of industrial wastewater flowing into the Damanganga adjacent to the CETP outfall pipe (see IT9059).

Table 3.1 Descriptions of samples collected from Vapi, Gujarat, India 1999.

3.3 Results and discussion

Results of the organic screening analysis are given in Tables 3.2a and 3.2b. List of all identified organic compounds are presented in Appendix 2 (Table 3.2c).

Results of the heavy metals analysis are presented in Tables 3.3a and 3.3b.

The common effluent treatment plant and bypass channel (IT9058-IT9060)

Both treated (IT9058) and apparently untreated (IT9059) wastewater samples were found to be heavily contaminated by organochlorine compounds. 18 and 35 organic compounds were isolated from samples IT9058 and IT9059 respectively. 12 organic compounds (67%) and 22 organic compounds (63%) were reliably identified in these samples. Organochlorine compounds represented the majority of reliably identified compounds in both samples: 10 and 11 of those were found in the sample IT9058 and IT9059 respectively. The classes of detected organochlorine compounds again included di-, tri-, tetrachlorobenzenes and chlorinated benzenamines. Diphenyl ether was also reliably identified in both samples. Additionally, sample IT9058 contained chlorinated a pyridine derivative and naphthalene. Sample IT9059 contained penta- and hexachlorobenzene, dibenzothiophene derivative and linear aliphatic hydrocarbons.

Groups of compounds reliably identified	Number of samples	Sample Codes
ORGANOHALOGEN COMPOUNDS		
Dichlorobenzenes	3	IT9058, IT9059, IT9060
Trichlorobenzenes	3	IT9058, IT9059, IT9060
Tetrachlorobenzenes	3	IT9058, IT9059, IT9060
Pentachlorobenzene	2	IT9059, IT9060
Hexachlorobenzene	2	IT9059, IT9060
Chlorinated benzenamines	3	IT9058, IT9059, IT9060
Chlorinated diazobenzenes	1	IT9060
Chlorinated pyridine derivatives	1	IT9058
PCBs	1	IT9060
POLYCYCLIC AROMATIC HYDROCARBONS		
Naphthalene and its derviatives	1	IT9058
PHENOLIC COMPOUNDS		
Cresols	1	IT9060
PHTHALATES		
DEHP	1	IT9060
OTHER AROMATICS		
Dibenzothiophene and its derivatives	1	IT9059
Benzaldehyde	1	IT9060
Benzothiazole derivatives	1	IT9060
Benzenamine and its derivatives	1	IT9060
Carbazole derivatives	1	IT9060
Organophosphorus compounds	1	IT9060
Diphenyl ether	3	IT9058, IT9059, IT9059
ALIPHATICS		
Linear alkanes and alkenes	2	IT9059, IT9060

Table 3.2a. Groups of organic compounds reliably identified in sediment and industrial wastewater samples collected in the vicinity of the Vapi Industrial Estate, Gujarat, INDIA

Sample Code	Compounds isolated	Number reliably identified (%)	Halogenated Compounds	PAHs	Phenolic compounds	Phthalates	Organosulphur compounds	Organonitrogen compounds	Organophosphorus compounds	Other aromatics	Aliphatics
IT9058	18	12(67%)	10	1	0	0	0	0	0	1	0
IT9059	35	22(63%)	11	1	0	0	1	0	0	1	11
IT9060	79	37(47%)	17	1	2	1	1	2	1	2	10

Table 3.2b . Results of organoscreen analysis of sediment and industrial wastewater samples collected in the vicinity of the Vapi Industrial Estate, Gujarat, INDIA

Sample Number	Cd (mg/kg)	Cr (mg/kg)	Co (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Zn (mg/kg)
IT9060	66.4	339.1	17.3	329.1	245.5	222.7	2.6	55.5	659.1

Table 3.3a Results of heavy metal analysis (expressed as mg/kg dry weight) Vapi, Gujarat, India 1999

Sample Number	Cd (ug/l)	Cr (ug/l)	Co (ug/l)	Cu (ug/l)	Pb (ug/l)	Mn (ug/l)	Hg (ug/l)	Ni (ug/l)	Zn (ug/l)
IT9058	50	90	<10	180	70	990	2	70	390
IT9059	4820	16500	170	17410	13190	3680	61	1090	53230

Table 3.3b Results of heavy metal analysis (expressed as ug/l) Vapi, Gujarat, India

Sediment sample IT9060 collected from the black stream of apparently untreated effluent contained more organic compounds which could be isolated and reliably identified than liquid sample IT9059 from this channel. Nonetheless, these included the compounds isolated from the liquid sample. 17 organohalogen compounds were reliably identified in the sediment sample including di-, tri-, tetra-, penta- and hexachlorobenzenes, chlorinated benzenamines, chlorinated diazobenzenes and PCBs. Other organic compounds found in this sample included cresols, a phthalate ester (DEHP), benzaldehyde, a benzothiazole derivative, N-alkylated benzenamines, a carbazole derivative, the pesticide chlorpyrifos and linear aliphatic hydrocarbons.

The range of organic compounds found in the sample IT9058 indicates that that CETP is ineffective in removing a wide range of toxic, persistent and bioaccumulative compounds. These, along with similar contaminants from the channel which appears to bypass the CETP (IT9059 and IT9060), are introduced into the Damanganga River. More information on toxicity, uses, production and environmental behaviour of key organic compounds is presented in Appendix 3.

Heavy metals analysis results show that both the effluent (IT9059) and the sediment (IT9060) collected are heavily contaminated with cadmium, chromium, copper, lead, mercury, nickel and zinc.

Levels of these metals in unpolluted rivers are extremely low; as described above, cadmium, chromium and mercury concentrations are usually less than 1 ug/l, whereas concentrations of copper, lead, nickel and zinc generally range from 20-50 ug/l (ATSDR 1997). This effluent contained mg/l levels of cadmium, chromium, copper, lead, nickel and zinc, along with concentrations of mercury usually only associated with discharges from the chlor-alkali and gold mining industries. These levels are thousands of times greater than those that would occur naturally. Therefore the continued discharge of this effluent is of very great concern, as is the disposal of the contaminated sludge that remains in the channel.

In addition, even the effluent that has been through the CETP (IT9058) contains high

levels of cadmium, and detectable levels of chromium, copper, lead, manganese, mercury, nickel and zinc. It is also probable that, were it to be sampled, the sludge at the bottom of the settling tank would be very heavily contaminated, as many of the metals will simply partition out of the water phase and into the sludges. No information is available on the fate of the contaminated CETP sludges.

Of all the samples collected and analysed for heavy metals in the current study, these were by far the most contaminated. Possible sources have been described above, and details on the environmental behaviour of these metals, and their toxicological properties can be found in the appendices at the end of this report.

4. Sarigam

4.1 Introduction

The town of Sarigam is situated approximately 15 kilometres south of Vapi. A separate industrial estate has been expanding in the area over recent years, and there have been reports by the local community of contamination of the ground water in the area. It has likewise been reported that some industries in the area pump untreated wastewater into the ground via bore-holes. The introduction of a CETP to handle the treatment of combined wastewaters from industries in the area has been proposed.

4.2 Description of sampling site

In order to determine the current levels of contamination of the ground water, a sample (IT9062) was taken from a bore-hole in the village of Sarigam, close to the Okarkhadi. The landowner reported that the bore-hole had been introduced to replace an open well, the water from which had become too contaminated for use. The same owner also reported that the quality of the water from the bore-hole had progressively decreased over a number of years.

Sample Number	Sample Description
IT9062	Groundwater collected from a 30-45 metre deep bore-hole in the town of Sarigam.

Table 4.1 Description of the sample collected from Sarigam, Gujarat, India 1999.

4.3 Results and discussion

Groundwater sample IT9062 collected from the village of Sarigam was analysed for volatile organic compounds (VOC) only. Organoscreen analysis of this sample showed the presence of five compounds: benzene, chlorobenzene, 1,3- and 1,4-dichlorobenzenes, and trichloroethene. Chlorinated compounds found in this sample have been quantified. The results of quantitative analysis are presented in Table 4.2.

Compound	MDL, ug/l*	Concentration, ug/l
Trichloroethene	5	20
Chlorobenzene	5	85
1,3-Dichlorobenzene	5	10
1,4-Dichlorobenzene	5	5

*Table 4.2 Concentration of volatile organochlorine compounds found in groundwater sample IT9062, Sarigam, Gujarat, India. * MDL – minimum detectable level*

As was mentioned in the description of the sampling in Sarigam, some industries in this area reportedly pump untreated wastewater into the ground via bore-holes. Thus, the appearance of the chemical contaminants found in the sample IT9062 may be of little surprise.

Industrial wastewater discharges, solid chemical wastes and dump leachates have been reported to be the major source of environment pollution by chlorinated benzenes (Howard 1989). Dichlorobenzenes can be moderately to tightly absorbed to particles when released to soil. Nevertheless, they have also been detected in various groundwaters around hazardous waste disposal areas indicating that these contaminants are able to leach (Howard 1989). Environmental release of chlorobenzene may also be expected to derive from its use as a solvent, either through fugitive emissions or volatilisation from pesticides for which it used as a carrier. Indeed, the results obtained from analysis of waste waters and sediments in this study indicate the high mobility, and ubiquitous distribution, of dichlorinated benzenes.

Trichloroethene, widely used as organochlorine solvent, may be introduced to the environment from direct manufacture discharges or it could be formed in groundwater which is contaminated with various other chlorinated solvents under anaerobic conditions i.e. through partial degradation (Hashsham *et al.* 1995, Loran & Olsen 1999, Butler & Hayes 1998, Miller *et al.* 1998). Chlorinated solvents have a density greater than water (CRC 1969) and groundwater plumes of these contaminants may form pools of residual solvent below the water table (Rivett *et al.* 1994). Chlorinated solvents could dissolve into groundwater from the existing immiscible phase and move with the general flow of groundwater. Modelling studies suggest that individual plumes may extend for several kilometres from their source (Burston *et al.* 1993). Chlorinated solvents may undergo reductive dechlorination under anaerobic conditions, though it has been reported that final transformation into methane and ethane is significantly retarded if several of these compounds are present together (Hughes & Parkin 1996a & b).

Contamination of the groundwater by chlorinated solvents is a world-wide problem and occurs in most cases in the vicinity of the industrial sites where these compounds are involved in the technological processes. Trichloroethene was the most ubiquitous pollutant in the investigation of groundwater pollution in the Coventry region (UK) (Lerner *et al.* 1993).

Quantitatively, only trichloroethene has exceeded the permissible levels set for drinking water in the sample of groundwater from Sarigram. According to the US Environmental Protection Agency (US EPA 1999) the levels of trichloroethene in drinking water should not be more than 5ug/l, which is four times lower that levels of this solvent found in the sample IT9062. Levels of 1,4-dichlorobenzene in the sample were lower than US EPA

limits. Nevertheless, the presence of these chemicals in unchlorinated groundwater is of concern. There are no limit values for chlorobenzene and 1,3-dichlorobenzene in drinking water, despite the fact that these chemicals are also hazardous. Animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994a) following exposure to chlorobenzene.

Benzene was the most abundant contaminant in this sample. Various industries use benzene to make other chemicals, such as styrene, cumene (for various resins), and cyclohexane (for nylon and synthetic fibres). Benzene is a component of crude oil and gasoline (ATSDR 1997) and is used for the manufacturing of some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides. Benzene in water and soil breaks down quite slowly. It is slightly soluble in water and can pass through the soil into underground water (ATSDR). Eating or drinking foods containing high levels of benzene can cause vomiting, irritation of the stomach, dizziness, sleepiness, convulsions, rapid heart rate, coma, and death. It is also found that benzene can cause cancer of the blood-forming organs. The US Department of Health and Human Services (DHHS) has determined that benzene is a known human carcinogen (DHHS 1998).

Further information on toxicity, common sources and environmental behaviour of organic compounds found in this study is given in Appendix 3.

Conclusions

Common effluent treatment plants (CETPs), which operate in Ankleshwar, Nandesari and Vapi Industrial Estates, have been promoted as the long-term solution to the problem of contaminated wastewater disposal in India. While such CETPs may well address part of the problem relating to high loading of surface waters with degradable organic material, BOD, solids and nutrients, these plants are fundamentally incapable of degrading or detoxifying the wide range of heavy metal and persistent organic contaminants which are also present. At best they can achieve a redistribution of these contaminants from the liquid to the solid sludge phase, reducing the immediate loading to surface waters but creating an additional contaminated waste stream which must be disposed of. In addition, many of the more volatile organic compounds (VOCs) may be released to the atmosphere before they can be degraded. For example, Haas and Herrmann (1996) estimate typical VOC losses from settlement ponds receiving effluents containing organic compounds in the mg or g per litre range, to be of the order of 10-100g per m per day.

Some of the less persistent organic compounds (e.g. 2,4-dichlorophenol or halogenated benzenamines) can be degraded by microbiological processes. However, to achieve acceptable and reproducible degradation of such compounds, specific process designs are generally required, including an inoculum of micro-organisms acclimated to survive with, and metabolise, the waste compounds in question (Fulthorpe & Allen 1995, Gonzalez *et al.* 1996). Many organisms appear to be capable of degrading chlorinated long-chain aliphatic compounds, but fewer strains can metabolise chlorinated aromatics (Mohn & Tiedje 1992). Complex and expensive plant, and long effluent residence times, are often required in order to achieve removal to an acceptable standard (Tunay *et al.* 1994). The upflow anaerobic sludge blanket plant is one such system (Duff *et al.* 1995).

Treatment systems are frequently subject to stimulation or inhibition as a result of changes in the flow rate and composition of wastewaters (Limbert & Betts 1995, Jin &

Battacharya 1996), or of changes in environmental variables such as process temperature and temperature of the inflowing effluent (Liss & Allen 1992). Activated sludge digestion appears to be particularly sensitive to changes in flow rate resulting from batch production processes (McAllister *et al.* 1993, Rebhun & Galil 1994). Shock loading with higher concentrations of particular compounds can perturb biodegradation processes in a manner which may be highly complex and difficult to predict (Lu & Tsai 1993, Torslov & Lindgaardjorgensen 1994, Strotmann *et al.* 1995). In addition, it should be noted that systems designed specifically to treat chemical wastes are frequently less efficient at achieving conventional biological treatment to reduce BOD, suspended solids and related variables.

In contrast to the specific bioreactor systems described above, a typical common effluent treatment plant, as in this study, would receive wastewaters from a wider range of industrial processes. This, by definition, would result in more complex and variable effluent composition and supply rates, rendering specific process design practically impossible (Eckenfelder & Musterman 1994). The mixing of highly complex waste streams, some of which may be hot and contain chemically active compounds, can result in the synthesis of new compounds in a largely unpredictable manner (see: Johnston *et al.* 1996). In addition, a large proportion of higher chlorinated organic compounds are highly resistant to biodegradation (Gruttner *et al.* 1994a, Middeldorp *et al.* 1996), while metal contamination can never be addressed through such processes, other than to scavenge them from the dissolved to the particulate fraction (Gruttner *et al.* 1994b). As a result, many of the most toxic and persistent components of chemical waste streams may simply pass through the CETP unmodified.

For example, the chlorinated benzenes are among the most persistent organochlorine compounds, being highly resistant to microbial degradation. Indeed, mono-, di- and tri-chlorobenzenes may be formed as persistent end-products from the biodegradation of other organochlorines (Middeldorp *et al.* 1996). In the study of the composition of domestic sewage sludge from the 1950s, which had been treated through anaerobic digestion, stored on site for five years and subsequently applied to farmland, di- and tri-chlorobenzenes were identified as the principle anthropogenic organic contaminants (Wang *et al.* 1992). Their presence is thought to have resulted initially from the use of dichlorobenzene in lavatory sanitizers.

In conventional biological sewage treatment systems, and simple industrial effluent treatment plants, chlorinated benzenes tend to bind tightly to the particulate fraction (Liljestrand & Lee 1991) on account of their poor water solubility. This results in their accumulation in sewage sludges or in sediments of receiving waters (e.g. Chapman *et al.* 1996). The presence of other organic solvents in suspension may, however, lead to higher solubility in the liquid phase. Under such conditions, typical of the mixed industrial effluents likely to enter a common treatment plant, dichlorobenzenes may inhibit the degradation of other compounds (Robertson & Alexander 1996), or increase the susceptibility of the bacterial consortium to toxic shock e.g. fluctuating concentrations of phenolics (Limbert & Betts 1995).

Biodegradation of chlorobenzenes, particularly higher chlorinated forms, is generally a slow process and one which requires careful selection of bacterial strains which are both resistant to, and capable of metabolising, these compounds (Limbert & Betts 1994). Other processes, such as high temperature hydrogenation (Gioia *et al.* 1994), are effective

in destroying di- and tri-chlorobenzenes but are expensive to install and run, and require considerable expertise to operate.

Englande (1994) emphasised the fact that there are no simple "off the shelf" solutions available for dealing with complex waste streams arising from diverse chemical manufacturing processes. Waste reduction strategies must form a central part of any waste management program, be it on the scale of a single process or plant, or of an industrial development region as a whole. Biological treatment plants may be effective in addressing certain limited physical, chemical and biological parameters, but can form only part of an overall waste management strategy. Brenner *et al.* (1994) and Belkin *et al.* (1994), discussing the strategy for the Ramat Hovav industrial complex in Israel, recognised the need to trace recalcitrant waste streams back to their origins and begin to address them at source. This necessarily involves detailed chemical characterisation of all the waste streams produced, leading to a re-evaluation of the raw materials and processes employed, in order to identify mechanisms for the reduction of use and release of persistent, toxic pollutants (Unden 1994). Ultimately it may be necessary to reformulate products in order to meet the long-term goal of elimination of priority pollutants at source.

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Appendix 1 Analytical methodology

1. Organic Analysis

1.1 Preparation of samples for Volatile Organic Compounds (VOCs) analysis

For volatile organic compound analysis, no sample preparation was required. The original sample was sub-sampled immediately after opening. Two portions of 10ml each were transferred into 20ml headspace vials and sealed with Teflon-lined vial caps. One sub-sample was used for the organic screen analysis to evaluate the whole range of the compounds in the sample. The second sub-sample was used for quantification of the detected compounds with an external standard method. For quantification of VOCs a standard calibration solution was prepared with the following compounds: chloroform, carbon tetrachloride, trichloroethene, tetrachloroethene, hexachloroethane, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trochlorobenzene, and 1,3,5-trichlorobenzene. All standard compounds were obtained from Sigma-Aldrich Co. Ltd./Supelco UK.

1.2 Preparation of samples for Organic Screen analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and clean up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105^0C, and rinsed three times with low haloform pentane.

Solid Samples

In preparation for analysis of extractable organic compounds, approximately 30g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15ml of pentane was added, followed by 5ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 20ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3ml. The concentrated extract was cleaned through a Florisil column, eluted with a 95:5 mixture of pentane: toluene, and evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at concentration 10mg/l to provide an indication of GC/MS performance.

Aqueous Samples

Prior to the extraction, samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10mg/l. 20ml of pentane were added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Both extracts were combined and cleaned up as described above for solid samples.

1.3 Chromatographic Analysis

Organic compounds were identified qualitatively and quantitatively using Gas Chromatography Mass Spectrometry (GC-MS).

Instrumentation was a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP Chem-Station data system and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 275,000 mass spectra combined with expert interpretation.

Instrumentation for the analysis of volatile organic compounds was a Hewlett Packard (HP) 5890 Series II gas chromatograph with HP 19395-A headspace sampler, interfaced with a HP Chem-Station data system and linked to a HP 5970 Mass Selective Detector operated in scan mode. Again, the identification of compounds was carried out using a combination of computer matching (against a HP Wiley 138 library of 138 000 mass spectra) and expert interpretation. Quantification of VOCs was performed in selective ion monitoring (SIM) mode using an external standard method, the target ions and qualifiers are presented in the table below.

Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater against HP Wiley 275 library or identification confirmed against standard compounds (using retention times and mass-spectra obtained during calibration) are assumed to give reliable identifications. Tentative identification refers to qualities between 51% and 90% against HP Wiley 275 library only. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

Chloroform	83	118
Carbon tetrachlorode	117	119
Trichloroethene	130	95
Tetrachloroethene	166	129
Hexachloroethane	117	201
Chlorobenzene	112	77
1,2-Dichlorobenzene	146	111
1,3-Dichlorobenzene	146	75
1,4-Dichlorobenzene	146	111
1,2,3-Trichlorobenzene	180	145
1,2,4-Trichlorobenzene	180	145
1,3,5-Trichlorobenzene	180	145

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2. Heavy Metal Analysis

2.1 Preparation of samples for heavy metals analysis

Solid samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. 0.5 g of sample was weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. Boiling tubes were then placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130 °C for five hours.

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A Standard Reference Material, BCR-143 (trace elements in a sewage sludge amended soil), certified by the Commission of the European Communities, Brussels, and a blank sample, were prepared with the batch of samples. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

Aqueous samples

On arrival, 100ml of sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). 50 ml was then transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130 °C for five hours. After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed.

2.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Following preparation, samples were analysed by ICP-AES, using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese, chromium, zinc, copper, lead, nickel, cobalt and cadmium. Two multi-element instrument calibration standard were prepared at a concentration of 10 mg/l. One in an acid matrix of 5% v/v hydrochloric acid and 5% v/v nitric acid (for solid samples), the other in an acid matrix of 10% v/v nitric acid (for aqueous samples). Calibrations were validated using quality control standards (8 mg/l), prepared internally from different reagent stocks. Samples exceeding the calibration range were diluted accordingly, in duplicate, and re-analysed.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two sets of calibration standards were prepared (different acid matrices, see above), at concentrations of 10 ug/l and 100 ug/l. Calibrations were validated using quality control standards (80 ug/l), prepared internally from different reagent stock. Samples exceeding the calibration range were diluted accordingly, in duplicate, and re-analysed.

Appendix 2

List of compounds reliably identified and groups of compounds tentatively identified in the samples (Tables 1.2c, 1.2d, 2.2c & 3.2c)

Sample Number: IT9043	Sample Number: IT9048	Sample Number: IT9049
Number of compounds isolated: 23	Number of compounds isolated: 164	Number of compounds isolated: 135
Sample type: Sediment	Sample type: Solid waste	Sample type: Industrial wastewater
Compounds reliably identified	**Compounds reliably identified**	**Compounds reliably identified**
6-Tridecene Benzene, hexachloro- Cyclododecane Cyclohexadecane Eicosane Heneicosane Nonadecane PCB-9	1,1'-Biphenyl 1,1'Biphenyl, 2,2'-dimethyl- 1,1'-Biphenyl, 2-amine- 1-Tetradecene Azulene, 2,4,6-trimethyl- Benzenamine, 2,3,4,5,6-pentachloro- Benzenamine, 2,4,6-tribromo- Benzenamine, 2,4,6-trichloro- Benzene, 1,1'-(1,2-ethenediyl)bis- Benzene, 1,1'-thiobis- Benzene, 1,2,3,4-tetrachloro- Benzene, 1,2,3,5-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,4,5-tetrachloro- Benzene, 1,2,4-tribromo- Benzene, 1,2,4-trichloro- Benzene, 1,2,4-trichloro-3-methyl- Benzene, 1,2,5-trichloro-4-methyl- Benzene, 1,2-dichloro- Benzene, 1,2-dichloro-3-methyl- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro- Benzene, 1,3-dichloro-5-methyl- Benzene, 1,4-dichloro- Benzene, 1,-bromo-4-methyl- Benzene, 1-chloro-2-methyl- Benzene, 2,4-dibromo-1-methoxy- Benzene, 2,4-dichloro-1-methyl- Benzene, hexachloro- Benzene, methoxy- Benzene, pentachloro- Benzene, pentachloromethyl- Benzene, trichloro(chloromethyl)- Benzenemethanol, alpha.-phenyl- Diazene, bis(2-methylphenyl)- Dibenzothiophene Dibenzothiophene, 1,6-dimethyl- Dibenzothiophene, 2,8-dimethyl- Dibenzothiophene, 3,4-dimethyl- Dibenzothiophene, 4,6-dimethyl- Dibenzothiophene,3-methyl- Docosane Eicosane Heneicosane Heptadecane Heptadecane Heptadecane, 2-methyl- Hexacosane Hexadecane Hexadecane, 2,6,10,14-tetramethyl- Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl- Naphthalene, 1,4,5-trimethyl- Naphthalene, 1,4,6-trimethyl- Naphthalene, 1,5-dimethyl- Naphthalene, 1,6,7-trimethyl- Naphthalene, 2,7-dimethyl- Naphthalene, 2-methyl Nonadecane Nonadecane, 2-methyl Nonadecane, 4-methyl- Octadecane Octadecanoic acid, 17-oxo-,methyl ester Octadecanoic acid, ethyl ester PCB-135 PCB-136 Pentacosane Pentadecane Pentadecane, 2,6,10,14-tetramethyl Tetracosane Tricosane Tricosane, 2-methyl Tridecane	1,1'-Biphenyl 1,1'-Biphenyl, 2,2'-dimethyl- 1,1'-Biphenyl, 2-methyl- 1,1'-Biphenyl, 3,3'-dimetnyl- 1,3 Butadiene, 1,1,3,4-tetrachloro- 1,3-Butadiene, pentachloro- 9H-Carbazole Benzenamine Benzenamine, 2,3,4-trichloro- Benzenamine, N-(phenylmethylene)- Benzenamine, N-ethyl- Benzenamine, N-methyl Benzenamine, N-propyl- Benzenamine, N-sulfinyl- Benzene, (1-methyldodecyl)- Benzene, (1-methylethyl)- Benzene, (methylthio)- Benzene, 1,1'-(1,2-ethanediyl)bis- Benzene, 1,1'-thiobis- Benzene, 1,2,3-trichloro- Benzene, 1,2,3-trimethyl- Benzene, 1,2,4-trichloro- Benzene, 1,2,4-trimethyl- Benzene, 1,2-dichloro- Benzene, 1,2-dichloro-4-ethenyl- Benzene, 1,2-dichloro-4-methyl- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro- Benzene, 1,4-dichloro- Benzene, 1-chloro-3-methyl- Benzene, 1-chloro-4-methoxy- Benzene, 1-methyl-2-(1-methylethyl)- Benzene, 1-methyl-3-propyl- Benzene, 1-methyl-4-(1-methylethyl)- Benzene, 1-methyl-4-(methylthio)- Benzene, hexachloro- Benzene, methyl(1-methylethyl)- Benzene, nitro- Benzene, pentachloro- Benzenemethanamine, N-phenyl- Benzenemethanol Benzenethiol Benzofuran, 2-ethyl- Benzonitrile Decane, 4-methyl- DEHP Diazene, (4-methylphenyl)phenyl- Diazene, diphenyl- Disulfide, diphenyl- Docosane Eicosane Ethanone, 1-phenyl- Junipene Naphtalene, 2-methyl- Naphthalene Naphthalene, 1-methyl- Octadecane, 3-methyl- PCB-10 PCB-13 PCB-19 PCB-24 PCB-3 Pentadecane Phenazine Pyridine, 4-methyl- Thiophene, 2-(p-methylstyryl)- Tricosane Tridecane Valencene
Groups of compounds tentatively identified	**Groups of compounds tentatively identified**	**Groups of compounds tentatively identified**
Aliphatic hydrocarbons Organosulphur compound	Aliphatic hydrocarbons Alkylbenzenes Biphenyl derivatives Chlorinated methoxybenzene Dibenzothiophene derivative Naphthalene derivative Organosulphur compounds Phenanthrene derivative	Acridine derivative Aliphatic hydrocarbons Alkylbenzenes Chlorinated benzenamine Naphthalene derivative Organonitrogen compounds Organosulphur compounds

Table 1.2c. List of organic compounds reliably and tentatively identified in sediment, solid waste and industrial waste water samples collected in the vicinity of the Ankleshwar Industrial Estate, Gujarat, INDIA

Sample Number: IT9050	Sample Number: IT9051	Sample Number: IT9052
Number of compounds isolated: 74	Number of compounds isolated: 96	Number of compounds isolated: 170
Sample type: Solid waste	Sample type: River water	Sample type: Sediment
Compounds reliably identified	**Compounds reliably identified**	**Compounds reliably identified**
1,1'-Biphenyl, 2-nitro- 1-Phenanthrenecarboxylic acid, 1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-(1-methylethyl)-, methyl ester Benzenamine, 2,3,4,5,6-pentachloro- Benzenamine, 2,3,4,5-tetrachloro- Benzene, 1-(1,1-dimethylethyl)-3,5-dimethyl- Benzene, 1-(1,1-dimethylethyl)-4-ethyl- Benzene, 1,2,3,5-tetrachloro-4,6-dimethyl- Benzene, 1,2-dichloro-4-(1-chloroethyl)- Benzene, 1,3-di-iso-propyl-5-methyl- Benzene, 1,4-dichloro-2,5-dimethyl- Benzene, 1-chloro-2-(1-chloroethyl)- Benzene, 4-bromo-1,2-dimethyl- Benzene, hexachloro- Benzene, trimethyl(1-methylethyl)- Benzonitrile, pentachloro- DBP DEHP DiBP Eicosane Ethanone, 1-(2,3,4-trimethylphenyl)- Ethanone, 1-(2,5-dimethylphenyl)- Heneicosane Heptadecane Octadecane Octyl phenol Phenanthrene Tricosane, 2-methyl-	1,1'-Biphenyl, 2,2'-dimethyl- 4-Pyridinol, tetrachloro- Benzenamine, 2,4,6-trichloro- Benzenamine, ar,ar,ar-tribromo- Benzene, 1,1'-thiobis- Benzene, 1,2,3,5-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,3-trimethyl- Benzene, 1,2,4-trichloro- Benzene, 1,2,4-trichloro-3-methyl- Benzene, 1,2-dichloro- Benzene, 1,2-dichloro-3-methyl- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro-2-methyl- Benzene, 1,4-dichloro- Benzene, 1,4-dichloro-2-methyl- Benzene, 1-chloro-2-methyl- Benzene, 1-chloro-4-methyl- Benzene, 1-ethyl-2-methyl- Benzene, 1-ethyl-3-methyl- Benzene, 1-methoxy-2-methyl- Benzene, 1-methyl-4-(phenylmethyl)- Benzene, 2,4-dichloro-1-methyl- Benzene, 4-ethyl-1,2-dimethyl- Benzene, trichloro(chloromethyl)- DEHP Diazene, bis(2-methylphenyl)- Dibenzothiophene, 3-methyl- Docosane Docosane, 11-decyl- Eicosane Eicosane, 2-methyl- Heptadecane Hexadecane Naphthalene Naphthalene, 1,4,6-trimethyl- Naphthalene, 1,5-dimethyl- Naphthalene, 1,6-dimethyl- Naphthalene, 1-methyl- Naphthalene, 2,3,6-trimethyl- Naphthalene, 2,7-dimethyl- Nonadecane Octadecane PCB-15 Pentacosane Pentadecane Tetracosane Thiophene, 2-(2-phenyl-1-propenyl)- Tritetracontane	1-Octadecene Benzenamine, 2,4,6-trichloro- Benzenamine, 2-chloro- Benzenamine, 2-methyl- Benzene, 1,1'-(1,2-ethanediyl)bis- Benzene, 1,1'-thiobis- Benzene, 1,2,3,4-tetrachloro- Benzene, 1,2,3,5-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,4,5-tetrachloro- Benzene, 1,2,4-trichloro- Benzene, 1,2,4-trichloro-3-methyl- Benzene, 1,2-dichloro- Benzene, 1,3,4-trichloro-6-methyl- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro- Benzene, 1,3-dichloro-5-methyl- Benzene, 1,4-dichloro- Benzene, 1-methoxy-4-methyl- Benzene, 1-methyl-2-(phenylmethyl)- Benzene, 2,4-dichloro-1-methyl- Benzene, hexachloro- Benzene, pentachloro- Benzyl benzoate Chlorpyrifos Cyclotetradecane Dithiophosphate, O,O,S-triethyl- Docosane Dodecane Dodecane, 2,6,10-trimethyl- Eicosane Ethanone, 1-(2,5-dichlorophenyl)- Heneicosane Heptadecane Hexacosane Hexadecane Nonadecane Nonadecane, 2-methyl- Octadecane PCB-3 Pentacosane Pentadecane Pentadecane, 2,6,10-trimethyl- Phenol Phenol, 2,5-dichloro- Phenol, 2-methyl- Phenol, 3-methyl- Phosphorodithioic acid, O,S,S-trimethyl ester Pyridine, 2,3,4,6-tetrachloro- Tetracosahexaene, 2,6,10,15,19,23-hexamethyl- Tetracosane Tetradecane trans-.beta.-Ocimene Tricosane Tridecane Undecane
Groups of compounds tentatively identified	**Groups of compounds tentatively identified**	**Groups of compounds tentatively identified**
Aliphatic hydrocarbons Alkylated phenols Alkylbenzenes Benzoic acid derivative Chlorinated benzenamine Chlorinated phenols Naphthalene derivative	Aliphatic hydrocarbons Alkylated phenols Alkylbenzenes Chlorinated toluenes Naphthalene derivative Organosulphur compounds	Aliphatic hydrocarbons Alkylated phenols Alkylbenzenes Benzenamine derivative Benzoyl chloride Chlorinated benzenamines Chlorinated toluenes Naphthalene derivative Organosulphur compounds

Table 1.2d. List of organic compounds reliably and tentatively identified in sediment, river water and solid waste samples collected in the vicinity of the Ankleshwar Industrial Estate, Gujarat, INDIA

Sample Number: IT 9053	Sample Number: IT 9054	Sample Number: IT 9055	Sample Number: IT 9056
Number of compounds isolated: 43	**Number of compounds isolated: 169**	**Number of compounds isolated: 34**	**Number of compounds isolated: 65**
Sample type: Industrial wastewater	**Sample type: Solid waste**	**Sample type: Solid waste**	**Sample type: Industrial wastewater**
Compounds reliably identified Benzene, (1-butylnonyl)- Benzene, (1-butyloctyl)- Benzene, (1-ethyldecyl)- Benzene, (1-ethylundecyl)- Benzene, (1-methyldodecyl)- Benzene, (1-methylnonyl)- Benzene, (1-methylundecyl)- Benzene, (1-pentylheptyl)- Benzene, (1-pentyloctyl)- Benzene, (1-propylnonyl)- Benzene, (1-propyloctyl)- Benzene, 1,4-dichloro- Naphthalene Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- **Groups of compounds tentatively identified** Alipohatic hydrocarbons Alkylbenzenes Chlorinated butene Organonitrogen compounds	**Compounds reliably identified** 1,3-Butadiene, 1,1,2,3,4,4-hexachloro- 1,3-Butadiene, 1,1,3,4-tetrachloro- 1,3-Butadiene, pentachloro- 1-Octadecanethiol Benzenamine, 2,3,4-trichloro- Benzene, 1,2,3,4-tetrachloro- Benzene, 1,2,3,4-tetramethyl- Benzene, 1,2,3,5-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,4-trichloro- Benzene, 1,2,4-trichloro-3-methyl- Benzene, 1,4,5-trichloro-2-methyl- Benzene, 1,4-dichloro- Benzene, 1-chloro-4-methyl- Benzene, 2-ethyl-1,3-dimethyl- Benzene, hexachloro- Benzene, pentachloro- Cyclododecane Decane Docosane Dodecane, 2,6,10-trimethyl- Eicosane Hexacosane Hexadecane Naphthalene, 1,4,5-trimethyl- Naphthalene, 1,4,6-trimethyl- Naphthalene, 1,4-dimethyl- Naphthalene, 1,5-dimethyl- Naphthalene, 1,6,7-trimethyl- Naphthalene, 1-chloro- Naphthalene, 1-methyl- Naphthalene, 2,3,6-trimethyl- Naphthalene, 2,6-dimethyl- Naphthalene, 2,7-dimethyl- Nonadecane Nonadecane, 2-methyl- Octadecane Pentacosane Pentadecane Pentadecane, 2,6,10,14-tetramethyl- Phenanthrene, 2,3-dimethyl- Phenanthrene, 2,7-dimethyl- Phenanthrene, 4-methyl- Tetracosane Tetradecane Tricosane Tridecane Tridecane, 2-methyl- **Groups of compounds tentatively identified** Aliphatic hydrocarbons Alkylbenzenes Biphenyl derivatives Chlorinated alkylbenzenes Indene derivatives Organonitrogen compounds Organosulphur compounds PAHs	**Compounds reliably identified** 1-Nonadecanol Benzene, 1,2,3-trichloro- Benzene, 1,2,4-trichloro- Benzene, 1,4-dichloro- Cyclotetradecane Tetratriacontane **Groups of compounds tentatively identified** Aliphatic hydrocarbons Alkylbenzenes Alkylphenols	**Compounds reliably identified** 1,1'-Biphenyl 9H-Fluorene Benzene, (1-ethyldecyl)- Benzene, (1-ethylnonyl)- Benzene, (1-methylnonyl)- Benzene, 1,2-dichloro- Benzene, 1,3-dichloro- Benzene, 1,4-dichloro- Docosane Eicosane Naphthalene Naphthalene, 1,4-dimethyl- Naphthalene, 1,5-dimethyl- Naphthalene, 1-methyl- Naphthalene, 2-methyl- Octadecane Pentacosane Phenanthrene Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- Tridecane **Groups of compounds tentatively identified** Aliphatic hydrocarbons Alkylbenzenes Indene derivatives PAHs

Table 2.2c. List of organic compounds reliably and tentatively identified in solid waste and industrial wastewater samples collected in the vicinity of the Nandesari Industrial Estate, Baroda, Gujarat, India

Sample Number: IT9058	Sample Number: IT9059	Sample Number: IT9060
Number of compounds isolated: 18	Number of compounds isolated: 35	Number of compounds isolated: 79
Sample type: Industrial wastewater	Sample type: Industrial wastewater	Sample type: Sediment
Compounds reliably identified Benzenamine, 2,3,4-trichloro- Benzenamine, 2,4,6-trichloro- Benzene, 1,2,3,5-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,4-trichloro- Benzene, 1,2-dichloro- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro- Benzene, 1,4-dichloro- Diphenyl ether Naphthalene Pyridine, 2,3,4-trichloro-6-methoxy- **Groups of compounds tentatively identified** Aliphatic gydrocarbons Alkylphenol derivative Brominated methoxybenzene	**Compounds reliably identified** Benzenamine, 2,3,4-trichloro- Benzene, 1,2,3,4-tetrachloro- Benzene, 1,2,3,5-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,4-trichloro- Benzene, 1,2-dichloro- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro- Benzene, 1,4-dichloro- Benzene, pentachloro- Benzene, hexachloro- Dibenzothiophene, 1-ethyl- Diphenyl ether Eicosane Heneicosane Hentriacontane Heptadecane Isolongifolene Naphthalene Octacosane Octadecane Tetradecane Tricosane **Groups of compounds tentatively identified** Aliphatic hydrocarbons Naphthalene derivative Organosulphur compounds	**Compounds reliably identified** 9H-Carbazole, 3-amino-9-ethyl- Benzaldehyde Benzenamine, 2,3,4-trichloro- Benzenamine, 2-chloro- Benzenamine, 3,4,5-trichloro- Benzenamine, 3,4-dichloro- Benzenamine, N-phenyl- Benzenamine, N-phenyl-2,6-dichloro- Benzene, 1,2,3,4-tetrachloro- Benzene, 1,2,3-trichloro- Benzene, 1,2,4-trichloro- Benzene, 1,2-dichloro- Benzene, 1,3,5-trichloro- Benzene, 1,3-dichloro- Benzene, 1,4-dichloro- Benzene, dichloro-4,4' diazo- Benzene, hexachloro- Benzene, pentachloro- Benzothiazole, 2-(methylthio) Chlorpyrifos DEHP Diphenyl ether Docosane Eicosane Heneicosane Hexadecane Junipene Naphthalene Nonadecane Octadecane PCB-139 PCB-15 Pentadecane Phenol, 2-methyl- Phenol, 3-methyl- Tetradecane Tricosane **Groups of compounds tentatively identified** Aliphatic hydrocarbons Alkylbenzenes Chlorinated pyridine Chlorinayed benzenamines Organonitrogen compounds Organosulphur compounds Phenol and its brominated derivative Phthalates

Table 3.2c. List of organic compounds reliably and tentatively identified in sediment and industrial wastewater samples collected in the vicinity of the Vapi Industrial Estate, Gujarat, INDIA

Appendix 3

Toxicological outlines for key organic compounds

Chlorinated Benzenes and Toluenes

The production of chlorinated benzenes is a multiple product operation achieved by direct chlorination of benzene in the liquid phase using a ferric chloride catalyst. Only limited control can be exerted over the final product mix. The distillation train used for separating the mixture has a limited resolving power and the distillates are always mixtures of close boiling isomers which can be further separated by crystallisation (see eg Bryant 1993). Distillation also gives rise to chlorinated tars.

12 chlorinated benzenes are possible, with substitution patterns as follows:

1 chlorine	monchlorobenzene,
2 chlorines	1,2-di-, 1,3-di- and 1,4-dichlorobenzenes
3 chlorines	1,2,3-tri-, 1,2,4-tri- and 1,3,5-trichlorobenzenes
4 chlorines	1,2,3,4-tetra-, 1,2,3,5,-tetra- and 1,2,4,5-tetrachlorobenzenes
5 chlorines	Pentachlorobenzene
6 chlorines	hexachlorobenzene.

Both technological changes and environmental concerns have severely affected the production of chlorobenzenes; today only monochlorobenzene and 1,2- and 1,4-dichlorobenzenes are manufactured in large quantities. These are often produced together, with the economically optimised reaction yielding approximately 85% monochlorobenzene, 10% 1,4-dichlorobenzene and 5% 1,2-dichlorobenzene. Monochlorobenzene yield can be increased to 90% by careful monitoring of the reaction mix density and recycling of unreacted benzene, but total elimination of dichlorobenzene formation is not economical. Should the primary interest be in the para- isomer, yield may be increased by use of a selective catalyst, or the mix can be further chlorinated to produce a mixture of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene. These two products can easily be separated by distillation (Bryant 1993, CEC 1986).

Mono- and di-chlorobenzenes.

Chlorobenzene, 1,2-dichlorobenzene and 1,3-dichlorobenzene are colourless liquids; 1,4-dichlorobenzene forms colourless crystals at room temperature (Ware 1988a & b).

One of the earliest uses of chlorobenzene was as an intermediate for the explosive picric acid during the first World War (CEC 1986). It is used as a solvent and as an intermediate in chemical synthesis. In the US in the 1980s, the predominant use was for the production of ortho- and para-chlorobenzenes. Theses are used as intermediates for rubber chemicals, antioxidants, dyes and pigments, pharmaceuticals and agricultural chemicals. The fungicide benomyl, and carbofuran and the parathion group of insecticides are all derived from chlorobenzene. One previously important use was in the manufacture of DDT. Chlorobenzene production has fallen due to the development of other routes to aniline and phenol and the restriction of DDT use. By various routes, chlorobenzene is also used for the manufacture of specialty silicones, Grignard reagents and catalysts (Bryant 1993).

Release to the environment is expected to derive from its use as a solvent, either through fugitive emissions or volatilisation from pesticides for which it used as a carrier. Thus, inhalation is thought to be a major route of exposure for humans since it is rarely if ever found in food. Mammalian metabolites are reported to be p-chlorophenol, p-chlorocatechol and p-chlorophenyl mercapturic acid. Human exposure causes CNS depression and respiratory tract irritation and animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994a). Canada has derived a TDI of 8.1ug/kg body weight/day; estimated exposures (0.05-0.14ug/kg/day) are considerably lower than this (Meek *et al.* 1994a).

Ware (1988b) reports human symptoms after exposure to DCBs, but does not distinguish between isomers. Effects reported are anaemia, skin lesions, vomiting, headaches, eye and respiratory tract irritation, anorexia, weight loss, yellow atrophy of the liver, blood dyscrasias, porphyria, and chromosomal breaks in blood samples. Animal experiments recorded liver and kidney damage to be the most frequent effects, though high doses caused CNS perturbation and death through respiratory depression. The dichlorobenzenes are bioaccumulative in algae, aquatic invertebrates and fish (Ware 1988b). All three have also been reportedly found in blood (Ware 1988b).

1,2-Dichlorobenzene is produced unavoidably in the production of monochlorobenzene, but it is also possible to maximise dichlorobenzene production to 98% of the reaction mixture using suitable catalysts or alternative production methods leading to specific isomers. It is used mainly in the production of dyes and pesticides after conversion to 1,2-dichloro- 4-nitrobenzene or dichloroaniline. Other uses include the solvent phase in the production of toluene di-isocyantes, production of deodorants and disinfectants and on a small scale as a heat transfer fluid. According to Meek *et al.* (1994b), the largest use is in degreasing for the metal and automotive industries.

Exposed laboratory animals exhibited hepatic, renal and haematological effects as well as lymphoid depletion of the thymus and spleen and multifocal mineralisation of both muscular and heart muscles (Ware 1988b, Meek *et al.* 1994b). Developmental toxicity was only observed at concentrations which were overtly toxic to the mother. Human toxicity data are sparse, but chromosomal aberrations, anaemia and leukemia have been reported (Meek *et al.* 1994b). Mammals metabolise 1,2-dichlorobenzene to phenols, catechols, most of which are excreted after conjugation with glucoronic or sulphuric acids. Mercapturic acids may also be produced. The primary metabolites in humans are conjugated phenols (Ware 1988b). 1,2-dichlorobenzene is found in air, food, breast milk and drinking water (Meek *et al.* 1994b). It is also toxic to higher plants, inducing abnormal mitosis (cell division) in onions (Ware 1988b).

1,3-Dichlorobenzene is growing in importance as a starting product in the manufacture of dyes, pesticides and pharmaceuticals. However, this has not yet reached commercial importance. There are some other small, specialised uses, but larger markets have not been developed, mainly because 1,3-dichlorobenzene only occurs as a minor constituent (approx 1%) of the technical dichlorobenzene reaction mix, and to produce it by other routes is expensive (Bryant 1993). Mammalian (and human) metabolism is as for 1,2-dichorobenzene above, but generally little is known about this 1,3-dichlorobenzene in comparison to the more commercially important dichlorobenzenes.

1,4-Dichlorobenzene (p-dichlorobenzene) is used largely in the production of deodorant blocks and room deodorants. It is also used as a moth control agent, as an insecticide and an intermediate for production of insecticides and dyes. An emerging market is in the manufacture of poly(phenylene sulphide) resin (PPS), and minor uses are as a germicide, fungicideand extreme pressure lubricant (Bryant 1993, CEC 1986). 1,4-dichlorobenzene is not spontaneously combustible and does not assist fire, but it is flammable nevertheless. It may be absorbed both through the inhalation of vapours, through the skin and though consumption of contaminated food. Human symptoms include damage to the liver, kidneys and lungs. Accidental poisoning of children, presumably who have eaten moth repellent was widespread in the 1970s (CEC 1986). Once absorbed, 1,4-dichlorobenzene is stored in the adipose tissue, and has been detected in human samples (CEC 1986, Ware 1988b). The metabolism of 1,4-dichlorobenzene by mammals varies from that of the other two isomers in that mercapturic acids are not formed. 1,4-Dichlorobenzene causes abnormal mitosis in higher plants. 1,4-Dichlorobenzene has been reported in human adipose tissue, as well as in blood (Ware 1988b).

Trichlorobenzenes

1,2,3- and 1,2,4-trichlorobenzene have been produced from the dehydrohalogenation of the unwanted isomers of the production of the pesticide 1,2,3,4,5,6-hexachlorocyclohexane. This is of limited application.

Environmental regulations have curbed the use and discharge of trichlorobenzenes to the environment, as least in Europe and the USA (Harper *et al.* 1992, Bryant 1993). Not surprisingly, therefore, little research appears to have been carried out in comparison with some other chlorobenzenes.

The general human population would probably receive their greatest exposure to trichlorobenzenes through inhalation. The toxicity of all three appear similar; they damage the liver, kidney and thyroid. There is some indication of slight fetotoxicity at high doses. There is little evidence of mutagenicity and too few data are available for the trichlorobenzenes to given a carcinogenicity classification (Giddings *et al.* 1994a). All three isomers are toxic to phytoplankton (Sicko-Goad *et al.* 1989a-d, Sicko-Goad & Andresen 1993a & b).

1,2,3-trichlorobenzene has been detected in air, drinking water, food and breast milk (Giddings *et al.* 1994a) as well as industrially polluted surface waters (Harper *et al.* 1992), though it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997). Little is known about its toxicity other than its ability to damage the liver, kidney and thyroid (Giddings *et al.* 1994a).

More information is available about 1,2,4-trichlorobenzene. According to Giddings *et al.* (1994a), only 1,2,4-trichlorobenzene has industrial application in Canada. It is imported for solvent and intermediate use. Environmental releases come from industrial discharges and from spillage of dielectric fluids. As mentioned above, it is toxic to the liver, thyroid and kidney. Liver and kidney weights and porphyrin excretion increase. In some studies, more severe liver damage has occurred, including necrotic and non-necrotic degeneration. 1,2,4-trichlorobenzene may be found in all environmental media, though there is

insufficient analytical data to tell how widespread contamination is and it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997).

Giddings *et al.* (1994a) report 1,3,5-trichlorobenzene air, drinking water, food, breast milk, though it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997). It can be found in association with industrial operations (Harper *et al.* 1992) including PVC industry (Johnston *et al.* 1993).

Tetrachlorobenzenes

Giddings *et al.* (1994b) reviewed toxicity and exposure data for the tetrachlorobenzenes. They are no longer used or produced in Canada and releases come only from dielectric fluid spills and long-range transport. 1,2,4,5-Tetrachlorobenzene used to be used in the production of 2,4,5-trichlorophenol on a large scale, but this use has now been largely discontinued. There are not expected to be large differences between the behaviour of the isomers. Uptake of 1,2,4,5-tetrachlorobenzene was studied in rainbow trout. It is not volatile enough to evaporate from water easily, and is accumulated by the fish, through its gills. Bioaccumulation depended upon the rate of activity and oxygen uptake of the fish, and only the low water solubility prevented significant toxicity occurring (Brauner *et al.* 1994).

The greatest exposure of the general population is probably through food. All isomers were found to affect the liver, kidney, thyroid and lungs, with 1,2,4,5-tatrachlorobenzene being the most toxic. Not enough information was available to classify tetrachlorobenzenes as to carcinogenicity.

In addition to the effects noted above, 1,2,4,5-tetrachlorobenzene has also caused changes in the spleen, thymus, lymph nodes and haematological parameters in animals (Giddings *et al.* 1994b). An increase in chromosomal aberrations was seen in workers exposed to 1,2,4,5-tetrachlorphenol at a pesticide manufacturing complex (Giddings *et al.* 1994b).

In rats, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene caused reduction in the number of live offspring at concentrations too low to adversely affect the mother (Giddings *et al.* 1994b).

All isomers have been detected in ambient air, drinking water and food and 1,2,3,4- and 1,2,3,5-tetrachlorobenzene have been identified in breast milk (Giddings *et al.* 1994b), though none of the isomers were detected in Canadian human adipose tissue (Hermanson *et al.* 1997).

Pentachlorobenzene

Giddings *et al.* (1994c) found that though no longer manufactured or used in Canada, pentachlorobenzene could still enter the environment through spillage of dielectric fluids or atmospheric transport. Animal studies demonstrate weight loss and effects on the liver, thymus, kidney, adrenal glands and digestive tract. Anaemia and malformation of sperm also occurred. There is some indication of fetotoxicity and developmental toxicity. The thyroid was impacted, with and thyroid hormone (free and total thyroxin) concentrations

reduced. Pentachlorobenzene cannot be assigned a carcinogenicity classification because of lack of data. Pentachlorbenzene accumulates in, and is toxic to algae (Sicko-Goad *et al.* 1989d).

Pentachlorobenzene has been detected in air, drinking water, food and breast milk (Giddings *et al.* 1994b), though according to Hermanson *et al.* (1997) it was found in less than 15% of human adipose samples collected in Ontario, Canada.

Hexachlorobenzene

Hexachlorobenzene (HCB) is a manufactured chemical, which was used as a wood preservative, as a fungicide for treating seeds, and as an intermediate in organic syntheses (Budavari *et al.* 1989). Additionally, hexachlorobenzene may be formed as an unwanted by-product in the synthesis of other organochlorine compounds high-temperature sources (Newhook & Meek 1994, Sala *et al.* 1999). The UNECE (1998) lists HCB alongside PCDD/Fs and PAHs as being the most important POPs emitted from stationary sources. HCB emissions from waste incineration, metallurgical industries and burning of chlorinated fuels are highlighted (UNECE 1998)(Annex V).

HCB is toxic to aquatic life, land plants, land animals, and humans. It is listed by the IARC as a Group 2B carcinogen, i.e. possible carcinogen to humans and also appears to be a tumour promoter. Hexachlorobenzene may damage the developing foetus, liver, immune system, thyroid and kidneys and CNS. The liver and nervous system are the most sensitive to its effects. Porphyria is a common symptom of HCB toxicity. High or repeated exposure may damage the nervous system, and can cause irritability, difficulty with walking and co-ordination, muscle weakness, tremor and/or a feeling of pins and needles on the skin. Repeated exposure, especially when skin effects occur, can lead to permanent skin changes, such as changes in pigmentation, tight, thickened skin, easy wrinkling, skin scarring, fragile skin, and increased hair growth, especially on the face and forearms (ATSDR 1997, Newhook & Meek 1994, van Birgelen 1998). Recent research (van Birgelen 1988) suggests that HCB has dioxin-like toxicity and that, based on a preliminary toxic equivalence factor (TEF) of 0.0001, HCB could contribute significantly to the dioxin-type toxicity of human milk based on PCB/PCDD/PCDF toxicity equivalents. In many countries, this could mean an increase of 10%-60%, but in countries with high HCB exposure levels, the effects could be even greater. In Spain and the Czech Republic, inclusion of HCB in total breastmilk TEQ estimates could lead to totals 6 times higher than based only on PCBs and PCDFs. Slovakia and India also have very high HCB levels; other countries (eg Austria) high levels in previous decades. It has been suggested that more epidemiological studies should be undertaken, especially in the most highly contaminated countries.

With the exception of occupational settings, almost all human exposure occurs via food. The greatest body of information on HCB toxicity to humans derives from an incident in Turkey between 1955 and 1959, when HCB-treated grain was made into bread. More than 600 people experienced porphyria cutanea tarda. Children of exposed women had skin lesions and 95% of them died at less than one year old. In the long term (20-30 years), some people continued to have abnormal porphyrin biochemistry and neurological, orthopaedic and dermatological symptoms persisted. Hexachlorobenzene is also thought to have caused porphyria cutanea tarda in populations exposed industrially and through

food (Newhook & Meek 1994). High concentrations of HCB were found in the air around a chlor-alkali and organochlorine manufacturing plant at Flix in Spain and in blood of workers and local residents (Sala *et al.* 1999, Grimalt *et al.* 1994). One study found a significant elevation in incidence of cancer of the thyroid, soft tissues and at unspecified sites in the men of the community (Grimalt *et al.* 1994) and the authors of one study stated that HCB exposure was associated with specific health effects in the most highly exposed subjects (Sala *et al.* 1999).

Once introduced into environment, HCB strongly absorb to soil materials and almost no desorption take place (Bahnick & Doucette 1988). It is bioaccumulative and biomagnifies. It can be measured in ambient air, drinking water, soil, food and breast milk (Newhook and Meek 1994).

HCB is one of twelve priority POPs intended for global action by the UN Environment Programme (UNEP) Governing Council. It is intended that HCB will be phased out worldwide under a convention currently being drawn up (UNEP 1995, 1997). Furthermore, HCB is included on Annex I of the Draft UNECE POPs Protocol under the Convention on Long-Range Transboundary Air Pollution (LRTAP)(UNECE 1998).
Within the EC, discharges of HCB are controlled as stipulated by EC Council Directive 86/280/EEC, which amends Directive 76/464/EEC, regarding pollution caused by certain dangerous substances discharged into the aquatic environment (EC 1986, 1976).

HCB is also included in the list of priority hazardous substances agreed by the Third and Fourth North Sea Conferences (MINDEC 1990, 1995), where continuous reduction of all hazardous substances was agreed with the ultimate aim of reducing environmental concentrations of hazardous substances to near background levels (synthetic substances to zero) within the next 25 years. The 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a) further reinforced these objectives. HCB is included on the OSPAR 1998 List of Candidate Substances, Annex 3 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

In addition, HCB is regulated under the 1995 Barcelona Convention, the Rotterdam (PIC) Convention and the IJ has called for all uses to be eliminated. See the Chapter on international legal instruments for further details.

Chlorinated Toluenes

The chlorinated toluenes (chloromethylbenzenes) occur in five chlorination stages of which four have several isomers. Some are produced by reacting liquid toluene with gaseous chlorine and the monochlorotoluenes are produced without substantial by-production of the dichlorotoluenes. Both batch and continuous methods of production are used. Since only a few of the isomeric chlorotoluenes can be produced economically by direct chlorination, others are produced by indirect syntheses.

They are principally manufactured in the United States, Germany and Japan with much of the production being consumed in captive applications. In the USA chlorinated toluenes were first manufactured by Hooker Electrochemical Co. and Heyden Chemical Corp. Heyden ceased manufacturing in the 1970s and Hooker were bought by Occidental, which is now the only producer in the USA (Lin & Krishnamurti (1993). World production is

estimated at several tens of kilotons for polychlorinated toluenes, while non captive end use sales account for between 0.1 and 1kt for o- and p- chlorotoluenes (Lin & Krishnamurti 1993).

Chlorination of both the aromatic ring and the side chain can take place. The commercially important ring substituted compounds are as follows:

2-Chlorotoluene (o-chlorotoluene)
4-Chlorotoluene (p-chlorotoluene)
2,4-Dichlorotoluene
2,6-Dichlorotoluene
3,4-Dichlorotoluene
2,3,6-Trichlorotoluene

Monochlorotoluenes

2-Chlorotoluene is usually thr predominat isomer generated by chlorination of toluene (about 70% under normal condition (Lin & Krishnamurti 1993. It is a raw material in the production of 2-chlorobenzyl chloride, 2-chlorobenzaldehyde and 2-chlorobenzoic acid. These are used as precursors in the production of dyes, pharmaceuticals, optical brighteners and fungicides. It is also used in the production of dichlorotoluenes and other chlorotoluenes for specialty applications.

3-chlorotoluene has similar solvent properties to 2-chlorotoluene, but little further information is available. It occurs at only a rate of about 1% on the chlorination of toluene and must be synthesised indirectly. During purification of technical mixes, it partitions into the p-chloro-toluene fraction (Lin & Krishnamurti 1993).

4-Chlorotoluene is used mainly to produce 4-chlorobenzotrichloride which as a precursor to 4-chlorobenzotrifluoride is important in the manufacture of dinitroaniline and diphenylether herbicides such as Trifluralin. Other side chain chlorinated derivatives are insecticides and dyes.

Monochlorotoluenes can be used to synthesis benzyl, benzal and benzotrichloride (see below); chlorinated benzaldehydes and chlorinated cresols.

Dichlorotoluenes

Chlorination of o-chlorotoluene yields all four possible dichlorotoluenes, with 2,5-dichlorotoluene making up some 60% of the reaction mix (Lin & Krishnamurti 1993). 2,4-Dichlorotoluene is used via its chlorinated side chain derivatives in the production of fungicides, dyes and pharmaceuticals, preservatives and peroxides.

The remainder of the commercially important ring substituted chlorotoluenes are used in small amounts to generate precursors for a variety of dyes and herbicides. Derivatives which are also chlorinated on the ring have little industrial significance.

Tri-, tetra- and penta-chlorinated toluenes.

These have relatively few industrial applications. 2,3,6-trichlorotoluene is used as a herbicide manufacturing intermediate (Lin & Krishnamurti 1993).

alpha-chlorinated toluenes

The important side chain chlorinated compounds, each of which has a majority end use, are:

Benzyl chloride ([chloromethyl]benzene)
Benzal chloride ([dichloromethyl]benzene)
Benzotrichloride ([trichloromethyl]benzene)

The IARC has classified benzyl chloride, benzal chloride, benzotrichloride and benzoyl chloride (C_6H_6COCl) as group 2A carcinogens on the basis of combined exposures.

Benzyl chloride

In 1989, the developed world had capacity to manufacture over 140,000 tonnes per annum of benzyl chloride. Monsanto had the largest capacity, with plants in US and Belgium. Other manufacturers were Bayer (West Germany), Tessenderlo Chemical (Belgium) and Akzo (USA). Velsicol ceased production in 1986 after poor market forecasts and other facilities were not utilising full capacity. Only a total 92,700 tonnes were manufactured in 1989; in the US only 54% of a possible 49,000 tonnes were produced (Lin & Bieron 1993). Benzyl chloride is largely utilised in the manufacture of benzyl butyl phthalate, a plasticiser for vinyl resins accounting for over two thirds of production. Other uses include the manufacture of benzyl alcohol, and quaternary ammonium compounds. Triphenylmethane dyes are also manufactured from this compound as are a number of flavour and perfume products, dyes, synthetic tannins, pharmaceuticals and resins (Lin & Bieron 1993, Saxena & Abdel-Rahman 1989). It has been identified as a constituent of oil refinery effluents (Saxena & Abdel-Rahman 1989).

Carcinogenicity of the chlorinated toluenes is discussed above. It is mutagenic and may damage the liver and heart and depress the central nervous system; developmental and foetal toxicity have also been reported. It is extremely irritating to the eyes, skin and respiratory system, causing pulmonary oedema (Lin & Bieron 1993). Because of its lacrymatory properties, it has been used as a chemical warfare agent (Saxena & Abdel-Rahman 1989).

Some 2,400 tonnes of benzyl chloride were amongst the waste dumped by Hooker Chemical in the Love Canal in New York State (Saxena & Abdel-Rahman 1989). Hooker Chemical bough the Canal (built by William T. Love in the 1890s as part of an unsuccessful hydroelectric project) in the 1940s. Between then and 1953, they filled it with an estimated 20,000 tonnes of drummed chemical wastes and in 1953 Occidental (who had bought Hooker in 1968) sold the site to the local school board for $1. A school and houses were built but residents suffered health problems including miscarriages and

birth defects. In 1978 pregnant women and children under two years of age were encouraged to leave the area and in 1980 the government offered to purchase the homes of another 710 families. After a cleanup costing tens of millions of dollars, the USEPA declared the site clean in 1990 and homes there were again offered for sale. However, environmental groups still believe that health hazards remain (Miller 1992).

Benzyl chloride is an irritant, dysregulator of liver bichemistry (Saxena & Abdel-Rahman 1989) and is mutagenic. After oral dosing, highest concentrations are found in the digestive tract, followed by the liver. Most was excreted in urine within three days (Saxena & Abdel-Rahman 1989).

Benzal chloride

Benzal chloride can be made by chlorination of toluene and is used mostly for the manufacture of benzaldehyde. It has a strong pungent odour, and is highly irritating, with lacrymatory properties (Lin & Bieron 1993). As discussed above, it is probably carcinogenic to humans in concert with other chlorinated aromatics.

Benzotrichloride

Further chlorination of benzal chloride produces benzotrichloride. It is important in the manufacture of a variety of compounds but is quantitatively mostly converted to benzoyl chloride. In 1988, of an estimated 68kt production capacity in the western world, approximately 31500 tonnes was realised. Bayer (FRG) has capacity of 14,000 tpa; Occidental, NY (USA)(20,000 tonnes) and Velsicol (USA)(11,00 tonnes)(Lin & Bieron 1993).

As with the other alpha-chlorinated toluenes, benzotrichloride is extremely irritating and lacrymatory (Lin & Bieron 1993). Its carcinogenic potential is discussed above.

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Hexachloro-1,3-butadiene

Hexachloro-1,3-butadiene (HCBD) is a colourless liquid with a turpentine-like odour. This compound is not found naturally in the environment. HCBD either commercially manufactured or is known to be a by-product of the manufacture of chlorinated hydrocarbons such as tetrachloroethene, trichloroethene, abd carbon tetrachloride (ATSDR 1997; US EPA, 1986, Johnston *et al.* 1994; Botta *et al.* 1996). It is always present in relatively small quantities (up to 5% and more of hexachlorobutadiene in the chlorolysis process of 1,2-dichloroethane for the production of carbon tetrachloride and tetrachloroethene), but, because of the huge production of volatile chlorinated solvents, the amounts of hexachlorobutadiene from the different processes are relevant (Botta *et al.* 1996). It is also reported as a contaminant in technical formulations of pentachlorophenol, used widely as a wood preservative (Goodrichmahoney *et al.* 1993). Hexachlorobutadiene was first prepared in 1877 by the chlorination of hexyl oxide (ATSDR 1997).

Hexachlorobutadiene is used as a chemical intermediate in the manufacture of rubber compounds (ATSDR 1997). Lesser quantities of hexachlorobutadiene are used as a solvent, a fluid for gyroscopes, a heat transfer liquid, hydraulic fluid, and as a chemical

intermediate in the production of chlorofluorocarbons and lubricants. Small quantities are also used as a laboratory reagent. In the international market, Russia is reported to be one of the major users of hexachlorobutadiene, where it is used as a fumigant on grape crops (ATSDR 1997).

Hexachlorobutadiene is a wide spread environmental contaminant. It can exist in the atmosphere as a vapour or adsorbed to airborne particulate matter. HCBD and it has been found in wastewater from chlorine industry, leachate from landfills and hazardous waste sites, and also in air, soils, surface water and sediments (ATSDR 1997; Santillo & Labounskaia 1997 a & b; Choudhary 1995). It has also been detected in fly ash from the inceniration of HCBD-containing hazardous wastes (Choudhary 1995).

Hexachlorobutadiene is toxic compound. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance (US EPA, 1986; Choudhary 1995). Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. Hexachlorobutadiene has high acute and chronic toxicity to aquatic life (US EPA, 1986).

Kidney was found to be a main target organ for HCBD (Jonker *et al.* 1996; Choudhary 1995). If ingested, HCBD concentrates in the kidney, interferes with fundamental processes of cell respiration and can, as a result of conjugation with other compounds in the body, react with DNA resulting in cell death or the development of tumours (Choudhary 1995; ATSDR 1997). Short and longer-term exposure to very low doses via food, induced kidney and liver damage in laboratory animals, with juveniles more at risk than adults. It was shown that human exposures to HCBD were associated with highly significant increases in a number of individual and summed bile acid measures in the study of the possible hepatic effects of different chlorinated compounds including HCBD (Driscoll *et al.* 1992)

The International Agency for Research on Cancer concluded that there was limited evidence of HCBD carcinogenicity in rats and classified HCBD as compound not classifiable as to human carcinogenicity (Group 3) (IARC 1999). The US Environmental Protection Agency considers HCBD to be a possible human carcinogen and has classified it as a Group C carcinogen (IRIS 1993).

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Alkylbenzenes

Alkylbenzenes are single-ring aromatic compounds containing one or more aliphatic side chains. While there are theoretically thousands of alkylbenzenes, the major products of commence and, therefore, those to which humans are most likely to be exposed included toluene (methylbenzene), ethylbenzene, cumene (isopropylbenzene), and three xylenes (1,2-, 1,3-, and 1,4-dimethylbenzene).

The occurrence of these compounds in the environment is due to their presence in crude oil and petroleum products. Alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful sewage markers (Chalaux *et al.* 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources. Monoaromatic (benzene derivatives) and polyaromatic hydrocarbons (PAHs) are considered to be the most toxic, and are known to be present at the highest concentrations during the initial phase of a crude oil spill (Overton 1994).

The acute toxicity of inhaled alkylbenzenes is best described as central nervous system (CNS) depression (Andrews & Snyder, 1986). Acute toxicity does not vary very much within the group. In animal models, relatively similar concentrations of inhaled alkylbenzene vapours were found to be lethal. Impaired reaction times and impaired speech are the two most commonly noted CNS effects (Klaassen *et al.* 1996). All alkylbenzenes mention above are irritating to the eyes and mucous membranes, can cause irritation and burning of the skin, and all are narcotics at high concentrations. Benzene itself is a known carcinogen. Chronic exposure can lead to bone marrow depression, which in a few cases, can progress to leukemia (Budavari *et al.* 1989).

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Chlorpyrifos

Chlorpyrifos belongs to the class of organic compounds called organophosphates (OPs). OP is the currently used generic term that includes all insecticides containing phosphorus. Other names used, but no longer in vogue, are organic phosphates, phosphorus insecticides, nerve gas relatives, and phosphoric acid esters. All organophosphates are derived from one of the phosphorus acids, and as a class are generally the most toxic of all pesticides to vertebrates. Because of the similarity of OP chemical structures to the "nerve gases", their modes of action are also similar. Their insecticidal qualities were observed in Germany during World War II in the study of the extremely toxic OPs nerve gases sarin, soman, and tabun. Initially, the discovery was made in search of substitutes for nicotine to control aphids (Metcalf 1995).

All OPs are esters of phosphorus having varying combinations of oxygen, carbon, sulphur and nitrogen attached, resulting in six different subclasses: phosphates, phosphonates, phosphorothioates, phosphorodithioates, phosphorothiolates and phosphoramidates. OPs are generally divided into three groups: aliphatic, phenyl, and heterocyclic derivatives. Chlorpyrifos is a heterocyclic organophosphate. Trade names for chlorpyrifos include Dursban, Lorsban, Loxiran, Zidil, Detmol, Perinex, Brodan, Eradex and Spannit (Galo & Lawryk 1991; RSC 1987). In pure form, chlorpyrifos is white crystal compound with a mild mercaptan odour. It is soluble in water to 2mg/l (Galo & Lawryk 1991). It is stable in neutral and weekly acidic media and hydrolysed by strong alkalis.

Chlorpyrifos is a broad-spectrum insecticide (Metcalf 1995). Chlorpyrifos is one of the most commonly used pesticides in the indoor environment today. It has been used as an active ingredient in agricultural formulations on wide range of crops including pome fruit, stone fruit, citrus fruit, nut crops, strawberries, figs, bananas, vines, vegetables, potatoes, beet, tobacco, soya beans, sunflowers, groundnuts, rice, cotton, lucerne, cereals, maize, outdoor ornamentals, turf and in forestry (RSC 1987). It is also used in flea collars and dips, animal sprays and shampoos, carpets, crack and crevice sprays, and for subterranean termite treatment. According to the US Environmental Protection Agency, 972 registered products contain chlorpyrifos for widespread uses for termite and roach control and home and garden use (US EPA 1997).

OPs have two distinctive features: they are generally much more toxic to vertebrates than other classes of insecticides, and chemically they are the most unstable or non-persistent. It is this latter characteristic that brought them into agricultural use as substitutes for the persistent organochlorines. Organophosphorus insecticides are reactive compounds and readily degrade by oxidation, hydrolysis, and in living organisms (Saint-Fort 1991). The half-life of chlorpyrifos in soil is 80-100 days. The main metabolite is 3,5,6-trichloro-2-pyridinol, which is subsequently degraded to organochlorine compounds and carbon dioxide (RSC 1987). In animals rapid metabolism occurs following oral administration of chlorpyrifos with the principal metabolites being 3,5,6-trichloro-2-pyridinol and

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monoethyl chlorpyrifos.

The OPs work by tying up or inhibiting certain important enzymes of the nervous system, namely cholinesterase (ChE). The enzyme becomes phosphorylated when it attached to the phosphorous moiety of the insecticide, a binding that is irreversible. This inhibition results in the accumulation of acetylcholine (ACh) at the neuron/neuron and neuron/muscle (neuromuscular) junctions or synapses, causing rapid twitching of voluntary muscles and finally paralysis and death of insects (Metcalf 1995). In higher animals the following effects associated with OPs poisoning are observed: muscarinic effects (nausea, salivation, lacrimation, and myosis), nicotinic effects (muscular fasciculations) and central nervous system effects (giddiness, tremulousness, convulsions and coma).

Thus, OPs are general biocides that are toxic to nearly all animals. The oral LD_{50} values (mg/kg) of chlorpyrifos to mallard and pheasants are 75 and 12 respectively (Metcalf 1995). Mullie & Keith (1993) reported that aerial application of chlorpyrifos resulted in temporary decrease in the abundance of birds, bird foods and cholinesterase levels in several bird spieces. Chlorpyrifos is also highly toxic to fish, bees and to beneficial parasites and predators (RSC 1987). The LC_{50} (96 hours) of chlorpyrifos for rainbow trout is 0.003mg/l. Even if it does not provoke any mortality, sublethal doses may be an important threat for species and population equilibrium by modifying physiological or behavioural parameters such as pheromonal communications (Delpuech *et al.* 1998). As a result, pollution of the environment by this insecticide could lead to a global modification of the biodiversity. Recent experimental data on rats suggest that chlorpyrifos may be a developmental neurotoxicant and that exposure *in utero* may cause biochemical and functional aberrations in foetal neurones as well as deficits in the number of neurones (Landrigan *et al.* 1999; Slotkin 1999; Brimijoin & Koenigsberger 1999).

At the present time, the greatest concern about uses of formulations containing chlorpyrifos relates to toxic effects on humans, especially children. An extensive and unusual pattern of birth defects including defects of brain, eyes, ears, palate, teeth, heart, feet, nipples and genitalia were reported in the study of four children exposed *in utero* to chlorpyrifos (Sherman 1996). Studies of indoor exposure to chlorpyrifos indicate that young children are at higher risks to the semivolatile pesticide than had been previously estimated (Davis & Ahmed 1998; Gurunathan *et al.*1998). The study showed that after a single broadcast use of the pesticide by certified applicators in apartment rooms, chlorpyrifos continued to accumulate on children's toys and hard surfaces 2 weeks after spraying. Based on the findings of this and other research studies, the estimated chlorpyrifos exposure levels from indoor spraying for children are approximately 21-119 times above the current recommended reference dose of 3µg/kg/day from all sources. Furthermore, it was found that chlorpyrifos is readily absorbed through the skin and decontamination procedures that rely on soap and water have low removal efficiencies (Fenske & Lu 1994).

The residual amounts of chlorpyrifos in certain food products are the subject of the European Community Legislation. Maximum levels of this pesticide residues in and on cereals and foodstuffs of animal origin are set by the Council Directive 93/57EEC (EEC 1993a) amending two previous documents (EEC 1986a & 1986b). Corresponding maximum levels of chlorpyrifos in certain products of plant origin including fruit and vegetables are set by the Council Directive 95/61/EC (EC 1995) which amended Council

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Phthalate esters

Phthalate esters are more often referred to as the phthalates. They are used in every major product category (Kemi 1994). 90% of all plasticizers is used in the production of soft PVC (Cadogan *et al.* 1993) but they are also used in inks and dyes (Jobling *et al.* 1995), which may be of particular relevance to the industrial estates under study. Ten to fifteen years ago DEHP and DBP were the phthalates produced in the greatest quantities (Menzert & Nelson 1986).

Phthalates are relatively persistent and are among the most abundant man-made chemicals in the environment (Jobling *et al.* 1995). They can also bioaccumulate to some degree, predominantly from food. The phthalates exhibit a wide range of toxic effects in laboratory animals. The summary below illustrates the scope of the toxicological problems associated with two of the three phthalates identified. Few data are available for DiBP.

DEHP can cause liver cancer in laboratory animals and has been classified as possibly carcinogenic to humans by the IARC and as a probable human carcinogen by the US Environmental Protection Agency. The US Department of Health and Human Services (DHHS) has determined that DEHP may reasonably be anticipated to be a carcinogen (DHHS 1998). In its scientific opinion expressed in November 1998, the European Commission's Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 1998) noted that the most sensitive effect of DEHP may be damage to the development of the testes, based on tests involving exposure of rats to relatively low concentrations both in the womb and for the first three weeks after birth. The Committee also judged that such testicular toxicity may have greater relevance for humans than carcinogenic effects.

Concern has also been raised about the ability of DEHP and some other phthalates to interact with hormone receptors in animals. Jobling and coworkers (1995) demonstrated that DEHP was able to bind to the human estrogen receptor, although it showed no significant estrogenic activity. Its potential to interfere with other aspects of the hormone system has not been fully investigated.

DEHP and DnBP can both damage the male and female reproductive systems (Chan & Meek 1994, ATSDR 1997). Both can damage sperm production (ATSDR 1997, Wine *et al.* 1997), impair reproductive success (Chan & Meek 1994, Ema *et al.* 1995, ATSDR 1997, Wine *et al.* 1997) and cause teratogenicity (malformation of the offspring) (Chan & Meek 1994, Ema *et al.* 1993; Ema *et al.* 1995, ATSDR 1997).

The liver and kidneys can be affected by DnBP (Chan & Meek 1994; ATSDR 1997) and DEHP (ATSDR 1997).

A group of phthalate esters including DnBP and DEHP has been found to have both acute (Adams *et al.* 1995) and chronic (Rhodes *et al.* 1995) toxicity to the representatives of freshwater and marine species, although toxicity may have been limited to some degree by the poor water solubility of these compounds. There was a general trend for the lower-molecular- weight phthalate esters (C-1 to C-4 alkyl chain lengths) to become more toxic with decreasing water solubility for all species tested.

Because of their recognised hazardous properties, these two phthalates (DBP and DEHP) are included on the OSPAR List of Chemicals for Priority Action (Annex 2 to the OSPAR Strategy with Regard to Hazardous Substances, OSPAR 1998).

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Biphenyl

1,1'-Biphenyl, also called diphenyl or biphenyl, is used in dye solvent mixtures (US EPA 1994). In the past, companies have used biphenyl as a heat transfer agent, as a raw material in the manufacture of polychlorinated biphenyls, and as a fungistat for oranges (applied to the inside of shipping containers or wrappers) (Edwards *et al.* 1991; Budavari 1989). Biphenyl has been found toxic to the experimental animals, causing CNS depression, paralysis and convulsions (Budavari 1989). Biphenyl has high acute toxicity and low chronic toxicity to aquatic life (US EPA 1994).

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Chlorinated biphenyls

Polychlorinated biphenyls (PCBs) are a group of synthetic organic chemicals that contain 209 individual compounds (known as congeners) with varying chemical contents and pattern of chlorine substitution. There are no known natural sources of polychlorinated biphenyls in the environment. PCBs are either oily liquids or solids and are colourless to light yellow in colour. They have no known smell or taste. PCBs enter the environment as mixtures containing a variety of individual components and impurities.

The polychlorinated biphenyls have been used in a wide variety of applications, including transformer oils, hydraulic fluids, plasticisers, 'kiss-proof' lipsticks and carbonless copy papers. They were also used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 1997).

PCBs were always sold as technical mixes rather than individual chemicals. de Voogt and Brinkman (1989) list some 46 trade names used for PCBs and PCB containing products. The Aroclor range manufactured by Monsanto was probably the most widely used. The most important PCB applications in tonnage terms were transformer oils and capacitors (de Voogt & Brinkman 1989). In transformer oils, the PCBs were mixed with chlorobenzenes (mainly trichlorobenzenes and tetrachlorobenzenes) as solvents (Swami *et al.* 1992, de Voogt and Brinkman 1989). PCBs may also be generated as a by-product particularly in the chlorine chemical industy. Such industries include the PVC industry, where waste EDC tars are contaminated, together with aqueous effluents, by dichlorobiphenyls.

The extensive body of information concerning the global cycling of PCBs has been accumulated in response to concerns about the environmental impact of these chemicals. PCBs are highly persistent. Although there is evidence of biodegradation in contaminated sediments (see: Brown & Wagner 1989) and some marine mammals appear to be able to selectively degrade some of the lower chlorinated congeners (Boon *et al.* 1987), the detoxification potential of these processes would appear to be rather limited. Indeed, Cummins (1988) has suggested that unless further escape of PCBs is prevented then the eventual extinction of marine mammals is a very real possibility.

Levels of PCBs in biological material may be several orders of magnitude higher than ambient. PCBs are bioconcentrated to a factor of 6000 for fish and 47000 for invertebrates (Jones *et al.* 1988). Train (1979) reports bioconcentration factors of between 2500 and 100,000.

PCBs can be absorbed through the skin as well as through ingestion and inhalation. For the general population today, food is the primary source, though dermal exposure may be

dominant amongst those directly handling PCBs or PCB-contaminated materials (Lees *et al.* 1987).

Safe (1993) lists the following symptoms of PCB toxicity:

enzyme induction
decreased vitamin A levels
lymphoid involution
thymic and splenic atrophy
immunosuppression
chloracne
alopecia
oedema
hyperkeratosis
blepharitis
hyperplasia of the epithelial lining of the extrahepatic bile duct
the gall bladder and urinary tract
hepatomegaly and liver damage including necrosis
haemorrhage
altered porphyrin metabolism
tumour promotion
altered levels of steroid and thyroid hormones
reproductive toxicity including menstrual irregularities, reduced conception, early abortion, excessive menstrual and postconceptual haemorrhage, anovulation, testicular atrophy, decreased spermatogenesis, teratogenesis and developmental toxicity.

In addition, low levels of PCBs caused behavioural impairment in monkeys (Rice 1999). Aroclor 1254 compromised the immune response of earthworms (Roch & Cooper 1991). Aroclors 1221, 1254 and 1268 all reduced in vitro fertilisation rates in mice. PCB 1254 was the most potent mix (Kholkute *et al.* 1994).

Kidney cancer has been reported in workers with known exposure to PCBs although insufficient data are available for statistical analysis and more research is called for (Shalat *et al.* 1989). In a review of epidemiological PCB research, cancer of the kidney and skin were marginally significant but the reviewers regarded the overall picture as inconclusive (Longnecker *et al.* 1997). Exposure of PCBs in an occupational setting exerts effects on the human CNS, with symptoms such as headaches, lassitude and slowed nerve signals (Rogan & Gladen 1992).

Invertbrates display a differential response to individual PCB congeners. In the aquatic snail, *Lymnaea stagnalis*, 2,2'-dichlorobiphenyl was substantially more toxic than the other congener under test, 4,4-dichlorobiphenyl (Wilbrink *et al.* 1987), being rapidly fatal to over 60% of the test animals (Wilbrink *et al.*, 1990) and inhibiting production of egg masses more rapidly.

Some congeners, or their metabolites, exhibit endocrine disruption, including both oestrogenicity and anti-oestrogenicity. In general, ortho-substituted PCBs are oestrogenic whereas coplanar PCBs are anti-oestrogenic as is 2,3,7,8-TCDD (Li *et al.* 1994). According to a recent review (Brouwer *et al.* 1999), PCBs may affect not only the oestrogen system, but also the androgen system, the thyroid hormone system, the retinoid

system, the corticosteroid system and several other endocrine pathways. In addition, effects on the thyroid system on wild populations of fish-eating birds and captive seals have been correlated with PCB exposure (Brouwer *et al.* 1999).

Ortho substituted (non-dioxin-like) PCBs have been found to have the greatest effects on neurochemical function. They were found to reduce dopamine synthesis and it was further established that the effects were caused by the congeners rather than their metabolites. 2,2'-dichlorobiphenyl (PCB 4) was the most potent congener (Seegal and Shain 1992).

The dioxin-like PCB 77 (3,3',4,4'-TeCB) also caused long-term changes in behavioural and neurochemical changes in laboratory animals, including alterations in dopamine function. This congener, however, did not accumulate in brain tissue in the same way as some ortho-substituted congeners, indicating that it operates via a second mechanism, or that it is a metabolite which is the active agent (Seegal & Shain 1992).

The effects of chronic exposure to PCBs in marine mammals has been found to include physical deformity and impairment of reproductive success (Reijnders, 1986). They have also been implicated in the outbreaks of disease amongst populations of seals and dolphins (see review by Gilbertson, 1989) suggesting that they may have a disruptive influence on immune capability.

The control of PCBs is addressed under most of the international legal instruments relating to organochlorines, *inter alia*, the Barcelona, Helsinki, Basel, Bamako, Rotterdam OSPAR and LRTAP Conventions and the International Joint Commission on the Great Lakes. In addition, PCBs are targeted for global production ban under the UNEP POPS Convention currently being drafted. Within the EC, applications for the PCBs were first restricted by Directive 76/769/EEC, which deals with the marketing and use of dangerous substances and preparations (EC 1976). It, and its amendment (EC 1991), restricted the applications of PCBs and their replacements, the PCTs.

EC regulations on disposal of PCBs, as set out in a 1996 Directive, dictate that the phase-out PCBs should be completed by 2010. Further, national enabling legislation should have been emplaced by March 1998. Several countries have missed this deadline and in mid 1999, the EC initiated action through the European Court of Justice against Germany, Greece, Spain, Portugal and UK for failing to implement the directive (ENDS 1999).
Within the European Community, PCBs are regarded as "blacklist substances" (Gardiner & Mance 1984) although no regulatory directive has yet been proposed. PCBs are also included in the proposed UK "red list" (Jones *et al.* 1988). The US Toxics Substances Control Act (TOSCA) designates wastes containing greater than 50ppm PCBs are designated as hazardous (Rogan 1995).

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Benzenamine and its derivatives

Benzenamine is an organonitrogen compound commonly referred to as aniline. In industry aniline is mainly produced by the reduction of nitrobenzene (ATSDR 1997). Also aniline may occur naturally in coal-tars. Aniline is one of the degradation products of the chemical benzidine, which was used in large amounts to produce azo dyes, sulfur dyes, fast color salts, naphthols, and other dyeing compounds primarily for textiles, paper, and leather products (ATSDR 1997; DHHS 1998). The use of benzidine declined because of its toxicity. This chemical was specified as known to be a human carcinogen by the US Department of Health and Human Services (DHHS 1998).

Aniline is toxic to human. Intoxication may occur from inhalation, ingestion or cutaneous absorption. Acute poisoning causes cyanosis, methemoglobinemia, vertigo, headache, and mental confusion. Chronic exposure to aniline results in anaemia, anorexia, weight loss and cutaneous lesions (Budavari *et al.* 1989). Cases of severe and nearly lethal toxic effects after dermal exposure to aniline-based dyes have been reported as early as 1886. These cases have involved mainly infants exposed to dye-stamped diapers and persons wearing freshly dyed shoes (Budavari *et al.* 1989).

Derivatives of aniline can be obtained directly from aniline by alkylation of nitrogen of the amine group or by halogenation. N-alkylation is carried out by passing a mixture of aniline over alcohol in the presence of a catalyst. Use of methanol will yield N-methylaniline (N-methyl substituted benzenamine). Under similar conditions ethanol will yield N-ethylaniline (Amini 1992). Halogenation of aniline with bromine and chlorine (in the presence of HCl in an anhydrous organic solvent) yields 2,4,6-tribromoaniline and 2,4,6-trichloroaniline respectively (Amini 1992). One of the known reactions of chlorinated anilines is the diazo coupling with chlorinated anisoles to produce o-hydroxyl PCB. Similarly the mechanism for synthesis of PBBs is the diazo coupling of brominated aniline (ATSDR 1997). Brominated anilines are used in the manufacture of azo dyes (Budavari *et al.* 1989).

When aniline is introduced into water it may undergo degradation under aerobic and denitrifying conditions. In aquatic environment aniline may also react with ozone to form N-substituted polyaromatic compounds: azobenzenes, azoxybenzenes, benzidines, phenazines, and aminodiphenylamines (Chan & Larson 1995). However, if aniline is released into soil it binds to soil particles and it is not readily desorbed or biodegraded (Kosson & Byrne 1995).

Substituted anilines can enter the environment in different ways. They are formed from the microbial metabolism of numerous pesticides, such as phenylurea, phenylcarbamate and acylanilide herbicides and nitroanilide fungicides (Hoff *et al.* 1985). They are also used industrially in the manufacture of dyes and may be released as pollutants in wastewater (Budavari *et al.* 1989). Chlorinated anilines can induce adverse effects on the environment and humans. Chloroanilines are found in waste effluents from tanning, cosmetic, PVC and pesticide industries (Paya-Perez *et al.* 1995; Johnston *et al.* 1996). Chloroanilines are

among the most toxic chemicals with an acute toxicity to earthworms (Paya-Perez *et al.* 1995).

Momo- and dichloroanilines

Monochlorinated anilines (o- and p-isomers) and aniline itself may be formed by the hydrolysis step from o- and p-chloroacetanilides in the sulfonamide production (Holm *et al.* 1995). Sulfonamides were used widely as an inexpensive pharmaceutical to control nocardiosis (acute or chronic lung infection) and toxoplasmosis (protozoan disease in central nervous system) and for veterinary purposes. The development of resistant bacteria, the discovery of side effects, and availability of other antibiotics have restricted the use of sulfonamides. Aniline, o- and p-chloroanilines, degradation products of sulfonamides, have been detected in landfill leachate and groundwater around one landfill in Denmark (Holm *et al.* 1995). Mono- and dichloroanilines have been also identified in wastewaters discharged form PVC manufacturing sites in Germany and the United Kingdom (Johnston *et al.* 1996).

3,4-Dichloroaniline is a product of hydrolysis of phenylurea herbicides such as 3-(3,4-dichlorophenyl)-1,1-dimethylurea, also known as Diuron, and 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea, known as Linuron (RSC 1987). 3,4-Dichloroaniline is toxic to fish. It was found that chronic exposure of zebrafish to this chemical resulted in cessation of egg production and this effect was irreversible (Ensenbach & Nagel 1997). Exposure of zebrafish to the mixture of 3,4-dichloroaniline and lindane accelerated the occurrence of this effect.

Hydrolysis of the fungicide Vinclozolin produces 3,5-dichloroaniline.

Trichloroanilines

2,4,5-trichloroaniline is a metabolite of microbial degradation of various phenylurea and phenylcarbamate herbicides (Hwang *et al.* 1985). In aqueous environment this compounds may undergo further degradation to CO_2 by both photochemical and microbial processes, but no degradation of 2,4,5-trichloroaniline is observed in darkness (Hwang *et al.* 1985).

2,3,4-trichloroaniline may bioconcentrate in fish and undergo further transformation with N-acetyl-2,3,4-trichloroaniline as a main product (de Wolf *et al.* 1992 & 1994). In anaerobic, flooded soils 2,3,4-trichloroaniline is subject to reductive dehalogenation which leads to formation of lower chlorinated anilines (2,3-dichloroaniline and 2-chloroaniline). However, heavy metals such as cadmium in water-soluble form may inhibit this process, particularly in the presence of high concentrations of humic acids (Pardue *et al.* 1996).

Tetra- and pentachloroanilines

Tetrachloroaniline and pentachloroaniline are the main degradation products of the fungicide pentachloronitrobenzene, also known as Quintozene, which is used against soilborne phytopathogenic fungi (Torres *et al.* 1996). Both of them may bioconcentrate in

fish (de Wolf *et al.* 1992 & 1994), however biotransformation processes such as oxidation and conjugation result in elimination of tetra- and pentachloroanilines from fish.

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Trichloroethene

Trichloroethene is a clear, colourless, heavy liquid with a pleasant, sweetish, chloroform-like odour, and a sweet burning taste. It easily evaporates at room temperature. Trichloroethene is non-flammable substance but it can decompose at high temperature in the air producing hydrochloric acid, phosgene and other compounds (CEC 1986). Other names of trichloroethene are trichloroethylene and ethylene trichloride.

Trichloroethene is a chlorinated solvent which was produced since the 1920s in many countries by chlorination of ethylene or acetylene (IARC 1995). Another method of producing trichloroethylene is by direct chlorination of ethylene dichloride to form trichloroethylene and tetrachloroethylene (ATSDR 1997). Oxychlorination of chlorinated wastes from PVC manufacturing (EDC tars) can be used to make chlorinated solvents including trichloroethene, but this method also results in the generation of large quantities of dioxins (EA 1997, ICI 1994). It has been used in vapour degreasing in 1920s, later it was introduced for use in dry cleaning but its use in this industry has declined sharply since the 1950s. In the 1990s, 80-90% of trichloroethene worldwide was used for degreasing metals (IARC 1995). Use for all applications in Western Europe, Japan and the United States in 1990 was about 225 thousand tonnes. Other uses include processes requiring strong solvent action to dissolve rubbers and resins and in the manufacture of paints, lacquers and adhesives and oils from animal and vegetable matter. The textile industry also uses trichloroethylene as a solvent in waterless dying and finishing operations (ASTDR 1997). It is also used as a chain terminator in the production of polyvinyl chloride, has also been used in fire extinguishing and fire retarding applications (CEC 1986).

Trichloroethene is photochemically reactive compound and it can decompose in the presence of free radicals. Stabilisers such as epoxides (including the carcinogen epichlorohydrin) or combinations of epoxides, esters and amines are added to commercial trichloroethene to prevent it becoming acidic towards equipment and degreased materials (CEC 1986).

Trichloroethylene is not thought to occur naturally in the environment. However, it is present in most underground water sources and many surface waters as a result of the manufacture, use, and disposal of the chemical (Hughes *et al.* 1994, WHO 1993, ATSDR 1997).

Trichloroethene was found at different levels in drinking water supplies: in Galicia (Spain) in range of concentrations between 1 and 11.6ug/l (Freiria-Gandara *et al.* 1992), in drinking water samples from Zagreb, Croatia, contained 0.69 to 35.90 ug/l (ATSDR 1997), and up to 212 ug/l in the drinking water from two villages in Finland (Vartiainen *et al* 1993). It was also detected in the breath of people after inhalation and dermal exposure to tap water contaminated with trichloroethene (Weisel & Jo 1996). The World Health Organisation guideline value for trichloroethene in drinking water is 70ug/l, assuming that this route provides 10% of exposure (WHO 1993). The maximum contaminant level (MCL) for trichloroethylene in drinking water set by US Environmental Protection Agency is 5 ug/l (US EPA 1999). Some surface waters have been found to contain more than 400ug/l of this contaminant (CEC 1986).

Trichloroethylene easily dissolves in water, and it remains there for a long time. Under anaerobic conditions (for example in ground water) trichloroethene may degrade to more toxic compounds including vinyl chloride (Klier *et al.* 1999, Su & Puls 1999, WHO 1993). Trichloroethene itself could be formed as a degradation product of another chlorinated volatile compound – 1,1,2,2-tetrachloroethane (Loran & Olsen 1999).

Trichloroethylene may absorb to particles in water, which will cause it to eventually settle to the bottom sediment (ATSDR 1997). Soil contamination by trichloroethene has been reported with concentration ranging from below 1mg/kg to approximately 1500mg/kg (Ho

et al. 1999). Trichloroethylene evaporates less easily from the soil than from water and may remain in soil for a long time.

Among the most heavily trichloroethene-exposed people are those working in the degreasing of metals, which are exposed by inhalation. Breathing large amounts of trichloroethylene may cause impaired heart function, coma, and death. Breathing it for long periods may cause nerve, lung, kidney, and liver damage. Inhaling small amounts for short periods of time may cause headaches, lung irritation, dizziness, poor co-ordination, and difficulty concentrating. Drinking large amounts of trichloroethylene may cause nausea, liver and kidney damage, convulsions, impaired heart function, coma, or death. Drinking small amounts of trichloroethylene for long periods may cause liver and kidney damage, nervous system effects, impaired immune system function and impaired foetal development in pregnant women, although the extent of some of these effects is not yet clear. Skin contact with trichloroethylene for short periods may cause skin rashes (ATSDR 1997).

Trichloroethene has been classified by International Agency for Research on Cancer in Group 2A (probably carcinogenic to humans) (IARC 1995). The most important observations are the elevated risk for cancer of the liver and biliary tract and the modestly elevated risk for non-Hodgkin's lymphoma. Trichloroethylene-contaminated groundwater may marginally increase a risk for non-Hodgkin's lymphoma. It has been shown to induce lung and liver tumours in various strains of mice (Fisher & Allen 1993, WHO 1993). It is also a weakly active mutagen in bacteria and yeast (WHO 1993).

Trichloroethene is in the first list of priority substances of the Commission Regulation (EC) No 1179/94 (EC1994) which is a part of the Council Regulation (EEC) No 793/93 on the evaluation and control of the risks of existing substances (EEC 1993).

Discharges of trichloroethene during several industrial processes (including production of tetrachloroethene and trichloroethene) and usage of trichloroethene for degreasing of metals are controlled by the European Community Legislation and special provisions are set relating to trichloroethene in the Council Directive 90/415 EEC (EEC 1990). The quality objective of 10ug/l for the aquatic environment (including inland surface waters, estuary waters, internal coastal waters other than estuary waters, and territorial waters) is set for trichloroethene in the same Directive.

Article 5(6) of the recent document (EC 1999) concerning limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations says that substances or preparations which, because of their content of volatile organic compounds classified as carcinogens, mutagens, or toxic to reproduction, shall be replaced as far as possible by less harmful substances or preparations within the shortest possible time.

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Butylated hydroxytoluene (BHT)

2,6-bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT), is frequently employed as an antioxidant in food products, rubbers, soaps and in the production of plastics and other petrochemical products (Jobling *et al.* 1995). It is also manufactured as an antiskinning agent in paints, varnishes and other surface finishes, and as an antioxidant. The use of BHT as an antioxidant in food has been associated with certain allergic reactions (Dean 1986). There is some evidence that BHT can act as a promoter of liver cancer, in combination with carcinogenic substances, through induction of abnormal liver metabolism (Williams *et al.* 1986). Additionally, BHT is one of the main degradation products of the herbicide Terbutol (2,6-di-tert-butyl-4-methylphenyl N-methylcarbamate) (Suzuki *et al.* 1995 & 1996).

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Appendix 4

Toxicological outlines for heavy metals

Zinc (Zn)

1. Natural Occurrence

Zinc is a relatively common metal, being 23rd in order of chemical abundance. It is found in the Earth's crust at an average concentration of 80 mg/kg, although some clay sediments and shales may contain higher concentrations (Alloway 1990, Salomons and Forstner 1984). It is not found naturally in it's pure form (as a lustrous, blue-white metal) but as a mineral (most commonly sphalerite, zinc sulphide), often associated with the ores of other metals (e.g. copper, lead and cadmium) (Kroschwitz and Howe-Grant 1995).

Natural sources of atmospheric zinc include wind-borne soil particles, emissions from forest fires and volcanoes, biogenic emissions and sea-salt sprays. The total amount of Zinc released to the atmosphere from natural sources is estimated at 45,000 tonnes / year, compared with an estimated anthropogenic load of 132,000 tonnes / year (Nriagu 1990).

2. Production, Use and Anthropogenic Sources

Once the zinc ore has been mined, broken and crushed, the Zinc minerals, on treatment with water and chemicals, can be concentrated efficiently. Surplus chemicals, washings and waste rock from these processes form the "tailings", and are separated and discharged. The concentrated ore is then heated in a furnace in the presence of air to produce Zinc oxide. This is then combined with coke or coal, and retorted to approximately 1,100°C to produce metallic Zinc. Alternatively, the roasted Zinc oxide can be leached with sulphuric acid, and electrolysed to produce Zinc of >99.9% purity, an increasingly popular practice (USPHS 1997, Kroschwitz and Howe-Grant 1995). Zinc can also be recovered from secondary sources i.e. "old" scrap, such as die castings and engraver's plates, and "new" scrap, such as drosses, skimmings, flue dust, and clippings (Kroschwitz and Howe-Grant 1995).

Zinc is one of the most extensively utilised "trace" metals (Nriagu 1990). It is most commonly employed as a protective coating for other metals e.g. galvanised steel, or as a component of bronze, brass and die-casting alloys. In addition, zinc salts are widely employed as wood preservatives, herbicides, catalysts, analytical reagents, vulcanisation accelerators for rubber, and stabilisers in PVC. They can also be found in ceramics, textiles, fertilisers, paints, pigments, batteries and dental, medical, and household products (USPHS 1997, Annema and Ros 1994, UNEP 1993, Budavari *et al.* 1989).

Estimates of anthropogenic emissions of Zinc are given in Tables 1-3 (Nriagu 1990, Nriagu and Pacyna 1988).

Source	Emission (thousand tonnes / year)
Non-ferrous metal production (Zn, Cu, Pb, Cd, Ni)	72.0
Steel and iron manufacturing	33.4
Energy production (coal and oil combustion)	16.8
Waste incineration (municipal refuse and sewage sludge)	5.90
Commercial uses (e.g. phosphate fertilisers, cement, paper, chemicals)	3.25
Mining	0.46
TOTAL	131.81

Table 1 World-wide atmospheric emissions of zinc from anthropogenic sources.

Source	Emission (thousand tonnes / year)
Manufacturing processes (metal, chemicals, paper, petroleum products)	85
Domestic wastewaters	48
Atmospheric fallout	40
Base metal mining and smelting	29
Electric power plants	18
Sewage discharges	17
TOTAL	237

Table 2 World-wide inputs of zinc into aquatic ecosystems

Source	Emission (thousand tonnes / year)
Discarded manufactured products	465
Agricultural, animal wastes, food wastes	316
Coal ashes	298
Atmospheric fallout	92
Urban refuse	60
Logging and wood wastes	39
Municipal sewage and organic waste	39
Solid wastes from metal fabrication	11
Fertilisers and peat	2.5
TOTAL	1322.5

Table 3 World-wide inputs of zinc to soils.

3. Environmental Levels, Contamination and Behaviour

Zinc is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of zinc far exceed those from natural sources, elevations above these natural, background concentrations are often found (see Table 5).

Zinc occurs in the environment primarily in the +2 oxidation state, either as the free (hydrated) zinc ion, or as dissolved and insoluble complexes and compounds (USPHS 1997). In soils, it often remains strongly sorbed, and in the aquatic environment it will predominantly bind to suspended material before finally accumulating in the sediment (USPHS 1997, Bryan and Langston 1992, Alloway 1990). However re-solubilisation back into an aqueous, more bioavailable phase is possible under certain physical-chemical conditions, e.g. the presence of soluble anions, the absence of organic matter, clay minerals and hydrous oxides of iron and manganese, low pH and increased salinity

(USPHS 1997). Zinc in a soluble form (e.g. sulphate or chloride, present in incinerator ash, or mine tailings) is far more likely to migrate through the environment than if it is bound to organic matter or present as an insoluble precipitate (e.g. as in sewage sludge) (USPHS 1997).

Environmental Matrix	Concentration	Reference
Seawater	<1 ug/l (open ocean) 0.3-70 ug/l (coastal and estuarine)	Bryan and Langston 1992. UNEP 1993
Freshwater	<50 ug/l	USPHS 1997
Drinking water	0.02-1.2 mg/l	USPHS 1997
Soil	10-300 mg/kg (50 mg/kg average)	Alloway 1990
Freshwater sediment	<100 mg/kg	USPHS 1997, Salomons and Forstner 1984
Marine Sediment	<100 mg/kg	Bryan and Langston 1992, UNEP 1993

Table 4 Background concentrations of zinc found in water, sediments and soil.

Site Description	Concentration	Reference
Restronguet Creek sediment, branch of the Fal estuary, UK. Receiving acidic drainage from past and present mining activities.	3000 mg/kg	Bryan and Langston 1992
Seawater, Restronguet Creek Seawater, polluted harbours in the Mediterranean	20-20460 ug/l 450 ug/l	Bryan and Langston 1992 UNEP 1993
Mediterranean coastal sediments (Venice Lagoon, River Ebro Delta, Izmir Bay, Kastela Bay, Gulf of Elefsis, Abu Kir Bay). Sites receiving large quantities of industrial and urban wastes	200-6200 mg/kg	UNEP 1993
Concentrations in surface soils in the vicinity of mines and smelters. Poland, UK, USA, Russia, Korea	11-10500 mg/kg 2040-50000 mg/kg 400-4245 mg/kg 329-25800 mg/kg	Dudka et al. 1995 Matthews and Thornton 1982 Dudka and Adriano 1997 Jung and Thornton 1996
River water, from sites receiving urban and industrial waste, USA	0.01-2.4 mg/l	USPHS 1997
Donana National Park, Spain. Contaminated river sediments close to mining sites	879-12200 mg/kg	Pain et al. 1998

Table 5 Zinc concentrations associated with sites of anthropogenic contamination.

Zinc is an essential element, present in the tissues of animals and plants even at normal, ambient concentrations. However if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results, with possible toxic effects (USPHS 1997).

4. Toxicity and Essentiality

Zinc is a nutritionally essential metal, having enzymatic, structural and regulatory roles in many biological systems (Goyer 1996, Aggett and Comerford 1995). Deficiency in humans can result in severe health consequences including growth retardation, anorexia, dermatitis, depression and neuropsychiatric symptoms (Aggett and Comerford 1995). At the other extreme, excessive dietary exposure, in both humans and animals, can cause gastrointestinal distress and diarrhoea, pancreatic damage and anaemia (USPHS 1997, Goyer 1996).

Due to the essentiality of zinc, dietary allowances of 15 mg/day for men, and 12 mg/day for women are recommended (USPHS 1997). Seafood provides a major source, and several species such as oysters, mussels, shrimps and crabs have bioconcentration factors ranging from several hundreds to several thousands (UNEP 1993). However, eating food containing very large amounts of zinc can induce the symptoms listed above. For example, animal studies involving doses 1,000 times higher than the RDA, taken over a period of month, resulted in anaemia and injury to the pancreas and kidney; and rats that ate very large amounts of zinc became infertile (USPHS 1997). Humans taking supplements at higher than recommended doses (400-500 mg/day) suffered severe gastro-enteritis (Abernathy and Poirier 1997); and humans who drank water from galvanised pipes, over a prolonged period, suffered irritability, muscular stiffness and pain, loss of appetite and nausea (UNEP 1993).

With regard to industrial exposure, metal fume fever resulting from the inhalation of zinc oxide fumes presents the most significant effect. Attacks usually begin after 4-8 hours of exposure, and last between 24-48 hours. Symptoms include chills and fever, profuse sweating and weakness (USPHS 1997, Goyer 1996).

Aquatic studies have shown that whilst zinc is not considered as being especially toxic to organisms, it is sometimes released into the aquatic environment in appreciable quantities. And in appreciable quantities, zinc can have a direct disrupting effect on the external cell membranes or cell walls of organisms, resulting in rapid mortality (UNEP 1993). However many studies now report that zinc is not only harmful at high concentrations, but also at lower sub-lethal concentrations, especially after prolonged exposure. For example, studies have shown that at concentrations as low as 15 ug/l, carbon fixation rates in natural phytoplankton populations were depressed. Others observed that the growth of cultured diatoms was inhibited at 20 ug/l (Bryan and Langston 1992). Effects on fertilisation and embryonic development in Baltic spring-spawning herring at low salinity were detected at only 5 ug/l (UNEP 1993); and the fertility of successive generations of harpacticoid copepod *Tisbe holothuria* was reduced by continuous exposure to only 10 ug/l (Verriopoulos and Hardouvelis 1988).

At slightly higher concentrations, studies investigating the effects of zinc on the hatching of brine shrimp (*Artemia salina*), noted that although increased concentrations of zinc did not affect development before emergence, the hatching stage of development was highly sensitive to, and heavily disrupted by, zinc (Bagshaw *et al* 1986). In addition, the inhibition of larval development was observed in the echinoderm (e.g. sea urchins and starfish) *Paracentrotus lividus* at a zinc concentration of only 30 ug/l (UNEP 1993). Shell growth in the mussel *Mytillus edulis* was effected at a concentration of 200 ug/l. With oxygen uptake, feeding and filtration rates were reduced at concentrations ranging between 750-2000 ug/l. Harmful effects on mollusc larva were seen to occur at levels as low as 40 ug/l (UNEP 1993).

Plant studies have shown that although an essential element for higher plants, in elevated concentrations zinc is considered phytotoxic, directly effecting crop yield and soil fertility. Soil concentrations ranging from 70-400 mg/kg are classified as critical, above which toxicity is considered likely (Alloway 1990). It was the observed phytotoxicity of zinc in sewage-sludge amended soils, that led several countries to formulate guidelines for sludge usage (Alloway 1990)

5. Legislation

Unlike mercury, cadmium and lead, zinc and its compounds are not found on National and International Lists of priority pollutants. However, whilst the reduction of anthropogenic sources of zinc does not require priority action, pollution of terrestrial and aquatic environments by zinc still needs to cease. Zinc is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more than 5 mg/l must be subjected to intensive physical and chemical treatment prior to use, with some degree of physical treatment still required for zinc levels of 0.5 mg/l.

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Zinc is included in List II, and as such water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Council Directive 78/659/EEC on the quality of fresh waters needing protection or improvement in order to support fish life. An Environmental Quality Standard of 0.3 mg/l is set.

European Council Directive 80/778/EEC relating to the quality of water intended for human consumption. Guide levels of 100 ug/l (for outlets of pumping and / or treatment works) and 5000 ug/l (after water has been standing for 12 hours in the piping / made available to the consumer) are set.

The Water Research Centre in the UK recommends the following Environmental Quality Standards for zinc: protection of freshwater salmonid fish 8-125 ug/l; protection of freshwater coarse fish 75-500 ug/l; protection of other freshwater life and associated non-aquatic organisms 100 ug/l; protection of saltwater fish, shell fish and associated non-aquatic organisms 40 ug/l (Mance and Yates 1984).

The USEPA recommends a maximum permissible concentration for drinking water of 5 mg/l (USPHS 1997), as do the WHO (1993) and the Bureau of Indian Standards (1995). For the protection of fresh and saltwater life, environmental quality standards of 570 and 170 ug/l respectively, are set. Furthermore, any release of more than 1,000 pounds (or in some cases 5,000 pounds) of zinc or its compounds into the environment (i.e., water, soil, or air) must be reported to EPA (USPHS 1997).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-250 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for zinc range from 1000-10,000 mg/kg, however resulting soil concentrations should not exceed 560 mg/kg (UK) or 300 mg/kg (EC, France, Germany) (Alloway 1990).

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Nickel (Ni)

1. Natural Occurrence

Nickel is the 24th most abundant element in the Earth's crust, with an average concentration of 75 mg/kg. However in some igneous rocks, clays and shales, higher concentrations can be found (Alloway 1990). Its commercially important ores are of two types, laterites, which are oxide and silicate ores, and sulphides (e.g. pentlandite) often associated with precious metals, copper and cobalt. The largest deposits of nickel are found in Canada, Cuba, Australia, CIS, and South Africa, with the most important single deposit (supplying over a quarter of the world's nickel), found in Canada, at Sudbury Basin (Greenwood and Earnshaw 1984).

Volcanic activity is the largest natural source of atmospheric nickel, followed by emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. It is estimated that the total amount of nickel released to the atmosphere from natural sources is 29,000 tonnes / year, compared with an estimated anthropogenic load of 52,000 tonnes / year (Nriagu 1990).

2. Production, Use and Anthropogenic Sources

Primary nickel is recovered from mined ore, which is first crushed, enriched and concentrated, prior to roasting and smelting operations; secondary nickel can also be recovered, from scrap metal. Alternatively, reduced nickel oxide ores can be electrolysed in the presence of nickel sulphate or chloride, to yield metal of 99% purity (Greenwood and Earnshaw 1984).

Nickel is a white-silver metal, hard but brittle, polishable, and a good conductor of both heat and electricity. It is most commonly used to form stainless and heat resistant steels, high nickel heat- and corrosion resistant alloys, alloy steels, super-alloys and cast irons. It is extensively used in electroplating, in the petroleum industry, in ceramics, in nickel-cadmium batteries and as an industrial catalyst, used for the hydrogenation of fats and methanation of fuel gases (USPHS 1997, Alloway 1990, Greenwood and Earnshaw 1984).

Estimates of anthropogenic emissions of nickel are given in Tables 1-3 (Nriagu 1990, Nriagu and Pacyna 1988):

Source	**Emission (thousand tonnes / year)**
Energy production (coal and oil combustion)	42.0
Steel and iron manufacture	4.47
Non-ferrous metal production (Ni, Cu, Pb)	3.99
Mining	0.80
Waste incineration (municipal refuse and sewage sludge)	0.35
TOTAL	51.61

Table 1 World-wide atmospheric emissions of nickel from anthropogenic sources.

Source	Emission (thousand tonnes / year)
Domestic wastewaters	62
Base metal mining and smelting	13
Electrical power plants	11
Sewage discharges	11
Atmospheric fallout	10
Manufacturing processes (metal, chemicals, paper, petroleum products)	7.4
TOTAL	114.4

Table 2 World-wide inputs of nickel into aquatic ecosystems.

Source	Emission (thousand tonnes / year)
Coal ashes	168
Agricultural and animal wastes	45
Atmospheric fallout	24
Discarded manufactured products	19
Municipal sewage and organic waste	15
Logging and wood wastes	13
Urban refuse	6.1
Fertilisers and peat	2.2
Solid wastes from metal fabrication	1.7
TOTAL	294

Table 3 World-wide inputs of nickel to soils.

3. Environmental Levels, Contamination and Behaviour

Nickel is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of nickel far exceed those from natural sources, elevations above these natural, background concentrations, are often found (see Table 5).

Environmental Matrix	Concentration	Reference
Seawater	0.1-0.5 ug/l	USPHS 1997, Law et al. 1994
Freshwater	<10-20 ug/l	USPHS 1997, Mance and Yates 1984
Freshwater sediment	45-65 mg/kg	Salomons and Forstner 1984
Soil	5-500 mg/kg (average 50 mg/kg) 40 mg/kg	USPHS 1997 Alloway 1990

Table 4 Background concentrations of nickel found in water, sediment and soil.

Nickel persists in water with an estimated residence time of 23,000 years in deep oceans and 19 years in near shore waters (Nriagu 1980). Its behaviour in the aquatic environment is governed by reactions with both soluble species and particulate matter. Complexes may be formed, with a variety of soluble organic and inorganic species. In addition, interactions with solid phases may occur. For example, direct adsorption onto particles such as clays; adsorption to or co-precipitation with hydroxides of iron and manganese, complexation with natural organic particles or direct precipitation. Studies have shown that nickel is a fairly mobile metal in natural waters, especially soluble at higher pH values. However generally speaking, concentrations of soluble nickel are low compared

with that associated with suspended and bottom sediments (USPHS 1997, Mance and Yates 1984).

Nickel is significantly bioaccumulated in some, but not all, aquatic organisms. Typical bioconcentration factors for significant bioaccumulators include marine phytoplankton <20-2000, seaweeds 550-2000 and algae 2000-40,000 (USPHS 1997).

Site Description	Concentration	Reference
Drinking water, near a large, open-pit mine, USA	200 ug/l	USPHS 1997
Seawater, coastal and estuarine sites of industrial and domestic discharges, UK	0.23-4.9 ug/l	Law et al. 1994
Sediment, Elsburgspruit-Natalspruit Rivers, South Africa (mining discharges and sewage)	54.5-890 mg/kg	Steenkamp et al. 1995
Soil, Sudbury Basin / Coniston, Canada (nickel mining and smelting)	100-3000 mg/kg 160-12300 mg/kg	Freedman and Hutchinson 1980 Hazlett et al. 1983
Soil, Upper Silesia, Poland (mining and smelting)	5-2150 mg/kg	Dudka et al. 1995
MSW incinerator ash, UK	45-2204 mg/kg	Mitchell et al. 1992

Table 5 nickel concentrations associated with anthropogenic contamination and waste.

In soils, the average residence time of nickel is estimated to be 2400-3500 years (Nriagu 1980), and although it is extremely persistent in soil, it is reasonably mobile and has the potential to leach through soil and subsequently enter groundwater (USPHS 1997, Alloway 1990).

4. Toxicity and Essentiality

Very small amounts of nickel have been shown to be essential for normal growth and reproduction in some species of animals, plants and micro-organisms. It is therefore assumed that small amounts may also be essential to humans, although the precise function of nickel is unclear (USPHS 1997, Alloway 1990). However, at the other extreme, there is sufficient evidence for the carcinogenicity of nickel and certain nickel compounds e.g. oxide, subsulphide, carbonate, acetate, carbonyl and hydroxide. The US Department of Health and Human Services, in its 8th Report on Carcinogens, therefore lists nickel and these compounds as Reasonably Anticipated to be Human Carcinogens (USPHS 1998). Whereas metallic nickel and its alloys are listed as possible human carcinogens (Group 2B), by the International Agency for Research on Cancer (1998).

Nickel is a respiratory tract carcinogen in workers in the nickel refining and processing industries. Here, individuals are frequently exposed to atmospheric levels in excess of 1 mg of nickel per cubic meter of air (USPHS 1997, Goyer 1996). Other serious consequences of long term exposure to nickel may include chronic bronchitis and reduced lung function (USPHS 1997). Whilst other studies have reported pregnancy complications in nickel-exposed workers, i.e. an increased rate of spontaneous abortion, and a higher incidence of birth malformations, including cardiovascular and musculoskeletal defects (Chashschin et al. 1994).

Allergic contact dermatitis is the most prevalent adverse effect of nickel in the general population (2-5% may be nickel sensitive). Here, people become sensitive to nickel when

jewellery or other nickel- containing objects are in direct contact with the skin. Once a person is sensitised to nickel, any further contact will produce a reaction. A rash at the site of contact is visible, and in some cases eczema may develop. Therefore, although none-sensitised individuals would have to ingest or inhale a large amount of nickel to suffer adverse health effects, sensitised individuals react adversely to far lower concentrations (USPHS 1997).

Few studies on the aquatic toxicity of nickel are available. However one toxicity study, carried out using temperate marine diatoms (Nitzschia closterium), juvenile banana prawns (Penaeus merguiensis), leader prawns (Penaeus monodon) and gastropods (Nerita chamaeleon), did find that survival and growth rates were effected by increased concentrations of nickel (Florence et al 1994).

5. Legislation

Unlike mercury, cadmium and lead, nickel and its compounds are not included on National and International lists of priority pollutants. However, whilst the reduction of anthropogenic emissions does not require priority action, pollution of terrestrial and aquatic environments by nickel still needs to cease. Nickel is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Nickel is included in List II, and as such, water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Community Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A Maximum Permissible Limit of 50 ug/l is set.

The Water Research Centre in the UK recommends the following Environmental Quality Standards for nickel: protection of freshwater fish 50-200 ug/l; protection of other freshwater life and associated non-aquatic organisms 8-100 ug/l; protection of saltwater fish, shellfish, other saltwater life and associated non-aquatic organisms 30 ug/l (Mance and Yates 1984).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-20 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for nickel range from 30-500 mg/kg. However soil concentrations should not exceed 30-50 mg/kg (EC, France, Germany) (Alloway 1990).

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Mercury (Hg)

1. Natural Occurrence

Mercury is a very rare metal, found in the earth's crust at concentrations frequently below 0.03 mg/kg (Alloway 1990). Cinnabar (mercury sulphide) is the only commercially important ore, and is found along lines of previous volcanic activity. The most famous and extensive deposits of cinnabar are in Spain (containing 6-7% mercury), with other deposits (<1% mercury) found in the CIS, Algeria, Mexico and Italy (USPHS 1997, Greenwood and Earnshaw 1984). Volcanic activity and biogenic processes are the largest natural sources of atmospheric mercury, followed by emissions from wind-borne soil particles, sea salt sprays and forest fires. It is estimated that the total amount of mercury released to the atmosphere from natural sources is 2500 tonnes / year, compared with an estimated anthropogenic load of 3550 tonnes (Nriagu 1990).

2. Production, Use and Anthropogenic Sources

Mercury ores are processed easily and inexpensively to produce metallic mercury. Due to the low boiling point of elemental mercury, refining can be achieved by heating the ore and condensing the vapour, a method that is 95% efficient, and yields mercury that is 99.9% pure (USPHS 1997).

Uses of mercury are extensive, due to its unique properties of fluidity, its high surface tension, and its ability to alloy with other metals. It is primarily used in the electrical industry in alkaline batteries, electric lamps, and wiring and switching devices, such as thermostats and cathode tubes. It is also used in the chemical industry as a catalyst used to form polymers (e.g. vinyl chloride and polyurethane), and as the cathode in the chlor-alkali electrolytic separation of brine to produce chlorine and sodium hydroxide (caustic soda). Mercuric oxide and mercuric sulphide are used as pigments in paints; and gold mining operations utilise mercury to extract gold from ores through amalgamation. Metallic mercury is used in dental restorations, and in medical equipment, such as thermometers and manometers. Until 30 years ago, mercury compounds were used extensively as pharmaceuticals and agrochemicals, e.g. as components of antiseptics, diuretics, skin lightening creams, laxatives, anti-syphilitic drugs, fungicides, bactericides, wood and felt preservatives. However, due to the high toxicity of mercury, most of these applications are banned in most parts of the World (USPHS 1997).

Estimates of anthropogenic emissions of mercury are given in table 1-3 (Nriagu 1990, Nriagu and Pacyna 1988).

Source	Emission (thousand tonnes / year)
Energy production (coal combustion)	2.26
Waste incineration (municipal refuse and sewage sludge)	1.16
Non ferrous metal production (Pb, Cu, Ni)	0.13
TOTAL	3.55

Table 1 World-wide atmospheric emissions of mercury from anthropogenic sources.

Source	Emission (thousand tonnes / year)
Manufacturing processes (metal, chemicals, petroleum products)	2.1
Atmospheric fallout	2.0
Electric power plants	1.8
Domestic wastewaters	0.30
Sewage discharges	0.16
Base metal mining and smelting	0.10
TOTAL	6.46

Table 2 World-wide inputs of mercury into aquatic ecosystems.

Source	Emission (thousand tonnes / year)
Coal ashes	2.6
Atmospheric fallout	2.5
Logging and wood wastes	1.1
Agricultural and animal wastes	0.85
Discarded manufactured products	0.68
Municipal sewage and organic waste	0.44
Urban refuse	0.13
Solid wastes from metal fabrication	0.04
Fertilisers and peat	0.01
TOTAL	8.35

Table 3 World-wide inputs of mercury to soils.

3. Environmental Levels, Contamination and Behaviour

Mercury is found at very low concentrations in many aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of mercury exceed those from natural sources, elevations above these natural, background, concentrations, can be found (see Table 5).

Due to the fact that mercury is the only metal that can exist as both a liquid and a vapour at ambient temperatures, its environmental behaviour differs from that of most other toxic elements (USPHS 1997, WHO 1989). mercury can exist in three valence states, Hg (0), Hg (I) and Hg (II). In the atmosphere, elemental mercury is by far the most common form, and, as a vapour, it is responsible for the long-range, global cycling of mercury. In addition, to a far lesser degree, mercury may be associated with particulates, which are removed by dry or wet deposition. Atmospheric inputs may be more significant in areas where other sources, such as contaminated rivers, are less important or non-existent (USPHS 1997, WHO 1992).

In the aquatic environment, mercury is most commonly found in the mercuric (II) state, and its fate, once released, is dominated by rapid adsorption to soluble and particulate organic material; followed by flocculation, precipitation and final accumulation in the bottom sediment. Because of the strength with which mercury is bound to sediment, exchange back to the water column is generally slight, although it can be accelerated in saline waters, and in the presence of high concentrations of sulphide (anoxic conditions) (USPHS 1997, Bryan and Langston 1992). Dredging or re-suspension of bed materials may cause short-term release of mercury, although levels of dissolved metal quickly return to pre-disturbance values. mercury accumulation from sediments may therefore be a dominant pathway for uptake in aquatic organisms and accounts for relatively high concentrations in deposit feeders, in both freshwater and marine systems (Bryan and Langston 1992).

Inorganic mercury can be methylated by micro-organisms, indigenous to soils, fresh water and marine sediments. The most common form of organic mercury is methylmercury (MeHg), which is soluble, mobile, and quick to enter the aquatic food chain. The selective retention of MeHg at each step in the food chain, relative to inorganic mercury, is related to its high lipid solubility, its long biological half-life, and the increased longevity of top predators (Bryan and Langston 1992). As a result, MeHg provides one of the rare examples of metal biomagnification in food chains (USPHS 1997, WHO 1989). For

example, concentrations in carnivorous fish at the top of freshwater and salt water food chains (e.g., pike, tuna, and swordfish) are biomagnified 10,000-100,000 times the concentrations found in ambient waters (USPHS 197). The significance of this bioaccumulation is that it is generally the most important source of human, non-occupational mercury exposure (USPHS 1997, WHO 1989).

Environmental Matrix	Concentration	Reference
Seawater (open ocean)	0.001-0.004 ug/l 0.02 ug/l	Bryan and Langston 1992, WHO 1989 USPHS 1997
Freshwater	<0.005 ug/l	USPHS 1997
Marine sediment	0.02-0.1mg/kg	WHO 1989
Freshwater sediment	0.2-0.35 mg/kg	Salomons and Forstner 1984
Soil	0.02-0.625 mg/kg	Alloway 1990, WHO 1989
Fish	<0.2 mg/kg	USPHS 1997

Table 4 Background concentrations of mercury found in water, sediments, soil and fish.

Environmental Matrix	Concentration	Reference
Marine sediment (Mersey estuary, UK)	6 mg/kg	Bryan and Langston 1992
Freshwater sediment (affected by gold mining, Brazil)	0.14-9.82 mg/kg	Reuther 1994
Soil (varying distances from chlor-alkali plant)	0.1-10 mg/kg	Gonzalez 1991, Alloway 1990
Fish (Madeira River, gold mining activities, Brazil)	<0.3-11.15 mg/kg	Barbosa et al. 1995

Table 5 mercury concentrations associated with anthropogenic contamination and waste.

4. Toxicity

Mercury is an extremely toxic, non-essential trace metal, having no biochemical or nutritional function. Biological mechanisms for its removal are poor, and, as mentioned above, mercury is the only metal known to biomagnify i.e. progressively accumulate though the food chain (WHO 1989).

Acute inhalation of high levels of mercury vapour may cause nausea, vomiting, diarrhoea, increases in blood pressure or heart rate, skin rashes, eye irritation, corrosive bronchitis and pneumonitis. And, if not fatal, may be associated with central nervous system (CNS) effects such as tremor or increased excitability (USPHS 1997, Goyer 1996). With chronic exposure, the major effects are on the CNS (tremor, spasms, loss of memory, increased excitability, severe depression personality changes, even delirium and hallucination), although renal damage, associated with chronically exposed workers, has also been shown (Ratcliffe *et al.* 1996, Goyer 1996). These effects have also been reported in animal studies (USPHS 1997)

Acute exposure to high levels of mercury salts, or chronic low-dose exposure, is directly toxic to the kidney (Zalups and Lash 1994). In addition, nausea and diarrhoea may result after swallowing large amounts of inorganic mercury salts, and some nervous system effects have also been recorded (USPHS 1997, WHO 1989).

Exposure to MeHg has resulted in permanent damage to the CNS, kidneys, and the developing foetus. The levels of MeHg that result in these effects are not usually encountered by the general population, however they were encountered by the population

of Minamata, in Japan, who were exposed to high levels of MeHg from eating contaminated fish and seafood collected from the Bay (USPHS 1997). Symptoms such as brain damage, numbness of extremities, and paralysis, along with the loss of hearing, speech and sight were reported (D'Itri 1991). However even today, the full range of neurological symptoms caused by the ingestion of MeHg in fish and shellfish has not been fully characterised, and the total number of Minamata Disease sufferers has not been determined (D'Itri 1991). Furthermore, whilst only the Japanese cases have been confirmed as Minamata Disease, other populations in Canada (from chlo-ralkali discharges) and Brazil (from gold mining) are potentially at risk. The problem of methylation of past and present inorganic mercury discharges continues, and the long retention time of mercury by sediments, delays the elimination of contamination for many years (Harada 1997, Barbosa 1997, Akagi *et al.* 1995, Bryan and Langston 1992, D'Itri 1991).

Studies on the aquatic toxicity of mercury are numerous, and again show that MeHg is more toxic than any of the inorganic forms. Invertebrate studies have reported significant reductions in the growth rate of the mussel *Mytilis edulis* at concentrations of 0.3 ug/l, with growth almost ceasing at 1.6 ug/l, and acute lethal effects observed at 25 ug/l (WHO 1989). In addition, changes in filtering activity, oxygen consumption, blood osmotic pressure, ciliary and valve activity have also been reported (Naimo 1995) In the American oyster *Crassostrea virginica* embryonic abnormalities were evident at concentrations of 5-10 ug/l. With survival rates of exposed clams and barnacles, copepods, shrimps and crustaceans all greatly effected by increased levels of mercury (WHO 1997, Bryan and Langston 1992).

Inorganic mercury is toxic to fish at low concentrations. The 96-h LC_{50}s vary between 33-400 ug/l for freshwater fish and are higher for salt-water fish; with organic compounds are more toxic to both (Bryan and Langston 1992, WHO 1989). Studies have reported a wide range of adverse reproductive effects in fish exposed to increased levels including prevention of oocyte development in the ovary and spermatogenesis in the testis of freshwater fish. Reductions in embryo survival and hatching success of *Fundulus heteroclitus* has also been reported, along with reductions in growth and an increase in deformities in trout (WHO 1989). Lack of movement and reduced food consumption, blindness and reduced respiratory rate have also been found in rainbow trout, bass and roach exposed to high levels of mercury (WHO 1989).

High incidences of abnormalities have also been observed in seabirds, abnormalities that seem to correlate with mercury residues in tissues. Even at sites apparently remote from contamination, elevated mercury concentrations have been determined in the liver and kidneys of fish eating seabirds, e.g. *Fulmarus glacialis*. Levels comparable with those suspected of producing sub-lethal effects, notably pathological changes to the kidney; and which have been shown to cause death in other species (Bryan and Langston 1992).

5. Legislation

European legislation on water quality and permissible environmental levels treat mercury as a priority pollutant i.e. legislation is concerned with the elimination of pollution caused by mercury and not just the reduction. For example:

Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more than 0.5 ug/l of mercury must be subjected to intensive physical and chemical treatment prior to use.

Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Mercury is included in List I, and as such water pollution caused by its presence should be eliminated.

Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A maximum permissible concentration of 1 ug/l is set.

Other drinking water standards include those set by the Bureau of Indian Standards (1 ug/l) (1995), the USEPA (2 ug/l) (USPHS 1997) and the WHO (1 ug/l) (1993).

In terms of soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-1 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for mercury range from 2-25 mg/kg. However resulting soil concentrations should not exceed 1-2 mg/kg (EC, UK, France, Germany) (Alloway 1990).

Finally, mercury is included in the list of priority hazardous substances agreed by the Third North Sea Conference (MINDEC 1990), Annex 1A to the Hague Declaration, and confirmed at the Fourth Conference in Esjberg, Denmark, in 1995 (MINDEC 1995). Here it was agreed that environmental concentrations of hazardous substances should be reduced to near background levels within the next 25 years. An objective further reinforced in the Sintra Statement at the 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a). Mercury has been selected for priority action, and as such as included in Annex 2 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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Copper (Cu)

1. Natural Occurrence

Copper was almost certainly one of the first three metals discovered (the others being gold and silver), and although opinion on the earliest use varies, 5000 BC is not an unreasonable estimate (Hong et al. 1996, Greenwood and Earnshaw 1984). Abundance in the Earth's crust is reported as ranging from 24-55 mg/kg (Alloway 1990), although higher levels are associated with some shales and clays (Thornton 1995). copper can occur in the elemental state, however it is found more commonly as a sulphide (copper pyrite), oxide (cuprite) or carbonate (malachite). The largest deposits of copper are found in the USA, Chile, Canada, the Commonwealth of Independent States, Zambia and Peru (Dudka and Adriano 1997, Alloway 1990).

Volcanic activity is the major source of copper released to the atmosphere, followed by emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. It is estimated that the total amount of copper released to the atmosphere from

natural sources is 28,000 tonnes / year, compared with an estimated anthropogenic load of 35,000 tonnes / year (Nriagu 1990).

2. Production, Use and Anthropogenic Sources

After the copper ore has been mined, crushed, enriched and concentrated, it is roasted at temperatures in excess of 1200 ° C, sintered and smelted. Alternatively copper can be recovered from secondary sources (i.e. scrap). This process is far less energy intensive, and therefore is playing an increasingly important role in terms of global copper production (UNEP 1993).

Copper is a highly malleable and ductile metal, as well as being an excellent conductor of heat and electricity. Its principal use is as an electrical conductor (copper cables and wires), however it is also widely employed in coinage alloys, in traditional alloys such as bronze (copper and tin), brass (copper and zinc) and Monel (copper and nickel), in corrosive-resistant and decorative plating, in munitions and in dental alloys. Its compounds are used as chemical catalysts, wood preservatives, algicides, fungicides, anti-fouling paints, disinfectants, nutritional supplements in fertilisers and feeds, in petroleum refining and as printing inks and dyes, (USPHS 1997, UNEP 1993).

Estimates of anthropogenic emissions of copper are given in Tables 1-3 (Nriagu 1990, Nriagu and Pacyna 1988).

Source	**Emission (thousand tonnes / year)**
Non-ferrous metal production (Cu, Pb, Zn, Cd, Ni)	23.2
Energy production (coal and oil combustion)	8.04
Steel and iron manufacturing	2.01
Waste incineration (municipal refuse and sewage sludge)	1.58
Mining	0.42
TOTAL	35.25

Table 1 World-wide atmospheric emissions of copper from anthropogenic sources.

Source	**Emission (thousand tonnes / year)**
Manufacturing processes (metal, chemicals, paper, petroleum products)	34
Domestic wastewaters	28
Base metal mining and smelting	14
Electric power plants	13
Sewage discharges	12
Atmospheric fallout	11
TOTAL	112

Table 2 World-wide inputs of copper into aquatic ecosystems.

3. Environmental Levels, Contamination and Behaviour

Copper is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, as anthropogenic emissions of copper exceed those from natural sources, elevations above these natural, background concentrations are often found (see Table 5).

Source	Emission (thousand tonnes / year)
Discarded manufactured products	592
Coal ashes	214
Agricultural and animal wastes	67
Logging and wood wastes	28
Urban refuse	26
Atmospheric fallout	25
Municipal sewage and organic waste	13
Solid wastes from metal fabrication	*4.3*
Fertilisers and peat	*1.4*
TOTAL	*970.7*

Table 3 World-wide inputs of copper to soils.

Environmental Matrix	Concentration	Reference
Seawater (English Channel, Irish Sea, North Sea)	0.35-4.0 ug/l (coastal) 0.14-0.9 ug/l (open ocean)	Law et al. 1994
Seawater (background)	0.1 ug/l	Sadiq 1992, Bryan and Langston 1992
Freshwater, UK	<20 ug/l	Mance et al. 1984
Soil	20 –30mg/kg	Alloway 1990
Marine sediment	10-30 mg/kg	UNEP 1993, Bryan and Langston 1992
Freshwater sediment	45-50 mg/kg	Salomons and Forstner 1984,

Table 4 Background concentrations of copper found in water, sediment and soil.

Copper may exist in natural waters either in the dissolved form as the cupric (+2) ion or complexed with inorganic anions or organic ligands (e.g. carbonates, chlorides, humic and fulvic acids). It may also be present as an insoluble precipitate (e.g. a hydroxide, phosphate, or sulphide) or adsorbed onto particulate matter. Alternatively it can be adsorbed to bottom sediments or exist as settled particulates. The relative concentrations of each of these forms is dependant upon a number of chemical parameters, including pH, salinity, alkalinity, and the presence of organic ligands, inorganic anions and other metal ions. However studies have frequently shown that the free +2 ion concentration is low, compared to the levels of copper associated with suspended and bottom sediments (USPHS 1997, Mance et al. 1984).

Site Description	Concentration	Reference
Seawater, Restronguet Creek, UK (receives acidic drainage from past and present mining activities)	>2000 ug/l	Bryan and Langston 1992
Sediment, Restronguet Creek	3000 mg/kg	Bryan and Langston 1992
Sediment, Izmir Bay (receives large quantities of industrial and domestic wastes)	33-866 mg/kg	UNEP 1993
Soil (nickel-copper mining and smelting, Sudbury, Ontario)	11-1890 mg/kg	Dudka et al 1995
Soil treated with copper fungicidal sprays	110-1500 mg/kg	Alloway 1990
MSW incinerator ash (UK)	296-1307 mg/kg	Mitchell et al. 1992

Table 5 copper concentrations associated with sites of anthropogenic contamination and waste.

In soils, copper has a high affinity for sorption by organic and inorganic ligands (e.g. humic and fulvic acids, hydroxides of iron, aluminium and manganese). However it can

also exist as soluble ions and complexes. copper in a soluble form is far more bioavailable and far more likely to migrate through the environment, that if it is bound to organic matter or present as an insoluble precipitate. Therefore, copper sulphate, or chloride, present in MSW incinerator ash or mine tailings, is far more bioavailable and migratory than the organically bound copper found in sewage sludge (USPHS 1997, Alloway 1990, Mance et al. 1984).

Copper is one of the most important, essential elements for plants and animals. However if plants and animals are exposed to elevated concentrations of bioavailable copper, bioaccumulation can result, with possible toxic effects (USPHS 1997).

4. Toxicity and Essentiality

Copper is an essential nutrient that is incorporated into numerous plant and animal enzyme systems, e.g. in humans, those involved in haemoglobin formation, carbohydrate metabolism, melanin formation, and cross-lining of collagen, elastin and hair keratin (USPHS 1997). Human deficiency is characterised by anaemia, resulting from defective haemoglobin synthesis (Goyer 1996). However at the other extreme, vomiting, hypotension, jaundice, coma and even death, can result from acute poisoning (USPHS 1997).

Therefore, even though copper is essential for good health, a very large single dose, or long term elevated exposure can be harmful. Inhalation of dust and vapours can irritate the nose, mouth and eyes, and cause headaches, dizziness, nausea and diarrhoea. Oral exposure to high levels can cause vomiting, diarrhoea, stomach cramps and nausea (USPHS 1997). Copper homeostasis plays an important role in the prevention of copper toxicity, in humans, terrestrial animals, and aquatic organisms. copper is readily absorbed from the stomach and small intestine; and after requirements are met, there are several mechanisms that prevent copper overload e.g. bile excretion, increased storage in the liver or bone marrow (USPHS 1997). However, failure of this homeostatic mechanism can occur in humans and animals following exposure to high levels of copper. This rare disease, known as Wilson's disease, is characterised by the excessive retention of copper in the liver and impaired copper excretion in the bile. Resulting in liver and kidney damage and haemolytic anaemia (USPHS 1997).

In addition to these effects, developmental and reproductive damage, following exposure to high levels of copper, has been seen in animals. However no such effects have been reported in humans (USPHS 1997).

Aquatic toxicity to copper is well studied, and there is experimental evidence that a considerable number of species are sensitive to dissolved concentrations as low as 1-10 ug/l (Bryan and Langston 1992). For example, studies have shown that at levels of 2 ug/l, the survival rate of young bay scallops was significantly effected; and in the embryos of oysters and mussels concentrations of 5 ug/l were seen to induce abnormalities. A similar concentration resulted in increased mortalities in populations of the isopod crustacean Idothea baltica (UNEP 1993, Bryan and Langston 1992, Giudici et al. 1989). Other studies have reported reductions in the survival, growth and fertility of amphipods and copepods (Conradi and DePledge 1998, UNEP 1993), and embryonic sensitivity in fish exposed to levels of 25 ug/l (UNEP 1993, Mance et al. 1984) Furthermore, a study of species diversity in benthic communities from Norwegian fjords, led to the conclusion that the

most sensitive animals were missing from sites where sediment-copper levels exceeded 200 mg/kg. In the UK, such concentrations are exceeded in a number of estuaries, including the Fal and the Tamar. Here, many species of bivalves, including some mussels, clams and cockles are absent, and at best distribution is severely limited. The toxicity of the surface sediment containing over 2000 mg/kg of copper, towards juvenile bivalves appears to be the reason (Bryan and Langston 1992).

5. Legislation

Unlike mercury, cadmium and lead, copper and its compounds are not included on National and International lists of priority pollutants. However, whilst the reduction of anthropogenic emissions does not require priority action, pollution of terrestrial and aquatic environments by copper still needs to cease. Copper is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more that 50 ug/l must be subjected to physical and chemical treatment prior to use.

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. copper is included in List II, and as such, water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.
European Council Directive 78/659/EEC on the quality of fresh waters needing protection or improvement in order to support fish life. An Environmental Quality Standard of 40 ug/l is set.

European Council Directive 80/778/EEC relating to the quality of water intended for human consumption. Guide levels of 100 ug/l (for outlets of pumping and / or treatment works) and 3000 ug/l (after water has been standing for 12 hours in the piping / made available to the customer) are set.

Other drinking water standards include those set by the Bureau of Indian Standards (1995) (50ug/l), the USEPA (1300 ug/l) (USPHS 1997) and the WHO (1000 ug/l)(1993)

The Water Research Centre in the UK recommends the following Environmental Quality Standards for copper: protection of freshwater fish, other freshwater life and associated non-aquatic organisms 1-28 ug/l; protection of saltwater fish, shellfish, other saltwater life and associated non-aquatic organisms 5 ug/l (Mance et al. 1984).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 1-100 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for copper range from 500-3000 mg/kg. However soil concentrations should not exceed 50-100 mg/kg (EC, France, Germany) (Alloway 1990).

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Chromium (Cr)

1. Natural Occurrence

Chromium is the 21st most abundant element in the Earth's crust, with an average concentration of 100 mg/kg. However in some igneous rocks, clays and shales, higher concentrations can be found (Alloway 1990). The only ore of chromium of any

commercial importance is chromite ($FeCr_2O_4$) which is produced principally in South Africa, Albania, Turkey, India and Zimbabwe. Other less plentiful sources are the ores crocoite ($PbCrO_4$) and chrome ochre (Cr_2O_3) (Mukherjee 1998, USPHS 1997, Alloway 1990, Greenwood and Earnshaw 1984). The gem stones, emerald and ruby, owe their colours to traces of chromium (Alloway 1990).

Emissions from wind-borne soil particles are the largest natural sources of atmospheric chromium, followed by emissions from volcanic activity, biogenic sources, forest fires and sea salt sprays. It is estimated that the total amount of chromium released to the atmosphere from natural sources is 43,000 tonnes / year, compared with an estimated anthropogenic load of 30,400 tonnes / year (Nriagu 1990).

2. Production, Use and Anthropogenic Sources

Chromium is produced in two forms. Firstly as ferrochrome, formed by the reduction of chromite with coke in an electric arc furnace (a low-carbon ferrochrome can be made using silicon, instead of coke, as the reductant). This iron-chromium alloy is used directly as an additive to produce chromium-steels, which are "stainless" and hard. Alternatively, following aerial oxidation of chromite, leaching, precipitation and reduction, chromium metal can be obtained (USPHS 1997, Greenwood and Earnshaw 1984).

Of the 10 million tonnes of chromium produced annually, about 60-70% is used in alloys, including stainless steel, which contains varying amounts of iron, chromium (10-26%) and nickel, depending on the properties required in the final product. The refractory properties of chromium (resistance to high temperatures) are exploited in production of refractory bricks for lining furnaces and kilns, accounting for approximately 15% of the chromate ore used. About 15% is also used in the general chemical industry, where chromium compounds are commonly used as tanning agents, textile pigments and preservatives, anti-fouling paints, catalysts, corrosion inhibitors, drilling muds, high temperature batteries, fungicides, wood preservatives, and in metal finishing and electroplating (USPHS 1997, Alloway 1990, Greenwood and Earnshaw 1984).

Estimates of anthropogenic emissions of chromium are given in Tables 1-3 (Nriagu 1990, Nriagu and Pacyna 1988):

Source	**Emission (thousand tonnes / year)**
Steel and iron manufacturing	15.6
Energy production (coal and oil combustion)	12.7
Cement production	1.3
Waste incineration (municipal refuse and sewage sludge)	0.8
TOTAL	30.4

Table 1 World-wide atmospheric emissions of chromium from anthropogenic sources.

3. Environmental Levels, Contamination and Behaviour

Chromium is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table 4). However, in areas associated with anthropogenic

emissions, ecosystem levels can far exceed natural, background concentrations (see Table 5).

Source	Emission (thousand tonnes / year)
Manufacturing processes (metal, chemicals, paper, petroleum products)	51
Domestic wastewaters	46
Sewage discharges	19
Base metal mining and smelting	12
Atmospheric fallout	9.1
Electric power plants	5.7
TOTAL	142.8

Table 2 World-wide inputs of chromium into aquatic ecosystems.

Source	Emission (thousand tonnes / year)
Discarded manufactured products	458
Coal ashes	298
Agricultural and animal wastes	82
Atmospheric fallout	22
Urban refuse	20
Logging and wood wastes	10
Municipal sewage and organic wastes	6.5
Solid wastes from metal fabrication	1.5
Fertilisers and peat	0.32
TOTAL	898.32

Table 3 World-wide inputs of chromium into soils.

Environmental Matrix	Concentration	Reference
Seawater (open ocean)	0.057-0.234 ug/l	Bryan and Langston 1992
Freshwater	1.30 ug/l	USPHS 1997
Drinking water	0.4-8.0 ug/l	USPHS 1997
Marine sediment	30-200 mg/kg	Bryan and Langston 1992,
Freshwater sediment / suspended particulates	1-500 mg/kg	USPHS 1997
Soil	<1-100 mg/kg 4-80 mg/kg	Alloway 1990 Dudka and Adriano 1997

Table 4 Background concentrations of chromium found in water, sediment and soil.

Environmental Matrix	Concentration	Reference
Marine sediment, Loughor Estuary (tin plate production) in South Wales	800 mg/kg	Bryan and Langston 1992
Marine sediment, Sawyer's Bay, New Zealand (tannery waste)	3700 mg/kg	Bryan and Langston 1992
Soil, chromium smelting, Japan	30-4560 mg/kg	Dudka and Adriano 1997
Soil, of sewage sludge amended farms, UK	138-2020 mg/kg	Alloway 1990
MSW incinerator ash, UK	44-1328 mg/kg	Mitchell et al. 1992

Table 5 chromium concentrations associated with anthropogenic contamination and waste.

Although many different oxidation states of chromium exist in the environment, only the trivalent (III) and hexavalent (VI) forms are considered to be of biological importance. In aquatic environments, chromium (VI) will be present predominantly in a soluble form. These soluble forms may be stable enough to undergo intra-media transport, however chromium (VI) will eventually be converted to chromium (III), by reducing species such

as organic substances, hydrogen sulphide, sulphur, iron sulphide, ammonium and nitrite (USPHS 1997, Kimbrough *et al.* 1999). This trivalent form is generally not expected to significantly migrate in natural systems. Instead, it is rapidly precipitated and adsorbed onto suspended particles and bottom sediments. However changes in the chemical and physical properties of an aquatic environment, can result in changes to the chromium (III)-chromium (VI) equilibrium (Richard and Bourg 1991).

Chromium (III) and (VI) have been shown to accumulate in many aquatic species, especially in bottom-feeding fish, such as the brown bullhead (*Ictalujrus nebulosus*); and in bivalves, such as the oyster (*Crassostrea virginica*), the blue mussel (*Mytilus edulis*) and the soft shell clam (*Mya arenaria*) (Kimbrough *et al.* 1999).

In soils, chromium (III) is relatively immobile due to its strong adsorption capacity onto soils. In contrast, chromium (VI) is highly unstable and mobile, since it is poorly adsorbed onto soils under natural conditions (Mukherjee 1998). Redox reactions (oxidation of chromium (III) to chromium (VI) and reduction of chromium (VI) to chromium (III)) are important processes affecting the speciation and hence the bioavailability and toxicity of chromium in soils. Oxidation can occur in the presence of oxides of manganese and iron, in fresh and moist (anaerobic) soils, and under slightly acidic conditions. Reduction can occur in the presence of sulphide and iron (II) (anaerobic conditions), and is accelerated by the presence of organic matter in the soil (Mukherjee 1998).

The importance of this lies in the fact that whilst chromium (III) is an essential trace elements in animals, chromium (VI) is non-essential and toxic at low concentrations. Thus, because oxidation processes can result in the formation of chromium (VI), anthropogenic activities that release either chromium (III) or chromium (VI) are equally non-desirable. Even if chromium (III) is discharged into the environment, there is no guarantee that it will remain in this chemical state. For example, the landfilling of chromium (III) tannery waste with other acidic industrial wastes, or domestic sewage, which on decomposition can yield acidic conditions, can result in the oxidation of chromium (III) to chromium (VI) (Mukherjee 1998, Outridge and Sheuhammer 1993, UNEP 1991, Richard and Bourg 1991).

4. Toxicity and Essentiality

Chromium (III) is considered an essential trace nutrient, required for glucose, protein and fat metabolism in mammals. Signs of deficiency in humans include weight loss and the impairment of the body to remove glucose from the blood (USPHS 1997, Goyer 1996). The minimum human daily requirement of chromium (III) for optimal health is not known, but a daily ingestion of 50-200 ug/day has been estimated to be safe and adequate. However, although an essential food nutrient, very large doses may be harmful (USPHS 1997).

Chromium (VI) is non-essential and toxic. Compounds are corrosive, and allergic skin reactions readily occur following exposure, independent of dose. Short-term exposure to high levels can result in ulceration of exposed skin, perforations of respiratory surfaces and irritation of the gastrointestinal tract. Damage to the kidney and liver have also been reported (USPHS 1997). In addition, the International Agency for Research on Cancer (IARC) classifies chromium (VI) compounds as known carcinogens (1998). Long-term occupational exposure to airborne levels of chromium higher than those in the natural

environment has been associated with lung cancer. Individuals at most risk include those in chromate-production industries and chromium pigment manufacture and use; and similar risks may exist amongst chromium-alloy workers, stainless steel welders, and chrome-platers (Kimbrough 1999, USPHS 1998).

The aquatic toxicology of chromium is also dependant upon speciation, with chromium (III) far less biologically available and toxic than chromium (VI). This has been observed in barnacles, *Balanus* sp., and in the polychaete *Neanthes arenaceodentata.* Experiments have shown that the number of offspring produced by the *Neanthes arenaceodentata* was reduced by exposure to 39 ug/l of dissolved chromium (VI) (Bryan and Langston 1992).

5. Legislation

Unlike mercury, cadmium and lead, chromium and its compounds are not found on National and International Lists of priority pollutants. However, whilst the reduction of anthropogenic sources of chromium does not require priority action, pollution of terrestrial and aquatic environments by chromium still needs to cease. chromium is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more than 50 ug/l must be subjected to physical and chemical treatment prior to use.

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Chromium is included in List II, and as such water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Community Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A Maximum Permissible Concentration of 50 ug/l is set.

Other drinking water legislation includes that set by the by the Bureau of Indian Standards (1995), the WHO (1993), and the USEPA (USPHS 1997). All of these set a guideline / recommended limit of 50 ug/l

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-100 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for chromium range from 200-1200. However resulting soil concentrations should not exceed 150 mg/kg (EC, France, Germany) (Alloway 1990).

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Cadmium (Cd)

1. Natural Occurrence

Cadmium is a relatively rare metal, being 67th in order of chemical abundance. It is found in the Earth's crust at an average concentration of 0.1 mg/kg (WHO 1992), although some sedimentary rocks, black shales and marine phosphates can accumulate higher levels (WHO 1992, Alloway 1990). It is usually found in association with the sulphide ores of zinc, copper and lead, and is obtained as a by-product during the processing of these ores. Volcanic activity is the major natural source of cadmium released to the atmosphere, followed by emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. It is estimated that the total amount of cadmium released to the atmosphere from natural sources is 1400 tonnes / year, compared with an estimated anthropogenic load of 7600 tonnes / year (Nriagu 1990).

2. Production, Use and Anthropogenic Sources

Cadmium is a by-product of zinc and lead mining and smelting, and is currently used primarily for the production of nickel-cadmium batteries (37%) and for metal plating (25%). It is also used in pigments for glasses and plastics (22%), as a stabiliser in polyvinyl chloride (12%), and as a component of various alloys (4%) (USPHS 1997, WHO 1992). Estimates of anthropogenic emissions of cadmium are given in Tables 1-3 (WHO 1992, Nriagu 1990).

Source	Emission (thousand tonnes / year)
Non-ferrous metal production (Zn, Cd, Cu, Pb, Ni)	5.43
Energy production (coal and oil combustion)	0.79
Waste incineration (municipal refuse and sewage sludge)	0.75
Manufacturing processes (steel, iron, phosphate fertilisers, cement)	0.60
TOTAL	7.57

Table 1 World-wide atmospheric emissions of cadmium from anthropogenic sources.

Source	Emission (thousand tonnes / year)
Manufacturing (metal, batteries, pigments, plastics)	2.4
Atmospheric fallout	2.2
Base metal mining and smelting	2.0
Domestic wastewaters	1.7
Sewage discharges	0.69
Electric power plants	0.12
TOTAL	9.11

Table 2 World-wide inputs of cadmium into aquatic ecosystems.

Source	Emission (thousand tonnes / year)
Coal ashes	7.2
Atmospheric fallout	5.3
Urban refuse	4.2
Agriculture and animal wastes	2.2
Discarded manufactured products	1.2
Logging and wood wastes	1.1
Fertilisers and peat	0.2
Municipal sewage / organic waste	0.18
Solid waste from metal fabrication	0.04
TOTAL	21.62

Table 3 World-wide inputs of cadmium to soils.

3. Environmental Levels, Contamination and Behaviour

Cadmium is a rare metal, found naturally as very low concentrations (see Table 4). However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background levels, are often found (see Table 5).

Environmental matrix	Concentration	Reference
Freshwater, groundwater, drinking water	<1 ug/l	USPHS 1997, WHO 1992
Seawater (open ocean)	0.02-0.12 ug/l	Sadiq 1992, Bryan and Langston 1992
Seawater (coastal)	0.01-0.17 ug/l	Bryan and Langston 1992
Marine sediment	<1 mg/kg	Sadiq 1992, Salomons and Forstner 1984
Estuarine sediment	0.2 mg/kg	Bryan and Langston 1992
River sediment	1 mg/kg	Salomons and Forstner 1984
Soil	0.01-2.0 mg/kg	USPHS 1997, Alloway 1990

Table 4 Background concentrations of cadmium found in water, sediment and soil.

Cadmium is more mobile in aquatic environments than most other metals. It is also bioaccumulative and persistent in the environment ($t^{1/2}$ of 10-30 years) (USPHS 1997). It is found in surface and groundwater as either the +2 hydrated ion, or as an ionic complex with other inorganic or organic substances. While soluble forms may migrate in water, cadmium in insoluble complexes or adsorbed to sediments is relatively immobile. Similarly, cadmium in soil may exist in soluble form in soil water, or in insoluble complexes with inorganic and organic soil constituents (USPHS 1997, WHO 1992). In soils, the agricultural use of phosphate fertilisers or cadmium-containing sewage sludge, can dramatically increase cadmium concentrations. Furthermore, cadmium is readily available for uptake in grain, rice and vegetables, and there is a clear association between the cadmium concentration in soil and the plants grown on that soil (Elinder and Jarup 1996, Cabrera *et al.* 1994, WHO 1992).

Site description	Concentration	Reference
Seawater, Restronguet Creek, UK (receives acid mine drainage from past and present mining activities)	50 ug/l	Bryan and Langston 1992
Sediment, Donana National Park, Spain (sites contaminated by mining waste)	2.4-38.6 mg/kg	Pain et al. 1998
Soils and sediments, Taiwan, close to a plastic stabiliser factory	0.22-1,486 mg/kg(soil) 134-4,700 mg/kg (sed.)	Chen 1991
Soil, Zn-Pb smelting, Upper Silesia, Poland	0.3-102 mg/kg	Dudka et al. 1995a
Soil, Cu-Ni mining site, Sudbury, Ontario	0.1-10 mg/kg	Dudka et al. 1995b
Garden soil, Shipham, UK (site of past Zn-Pb mining)	360 mg/kg (max.)	Alloway 1996
MSW fly ash (UK incinerators)	21-646 mg/kg	Mitchell et al. 1992

Table 5 cadmium concentrations associated with sites of anthropogenic contamination and waste.

When present in a bioavailable form, both aquatic and terrestrial organisms are known to bioaccumulate cadmium. Studies have shown accumulation in aquatic animals at concentrations hundreds to thousands of times higher than in the water (USPHS 1997). With reported bioconcentration factors ranging from 113 to 18,000 for invertebrates and from 3 to 2,213 for fish. Cadmium accumulation has also been reported in grasses and food crops, and in earthworms, poultry, cattle, horses, and wildlife (USPHS 1997, WHO 1992). Evidence for biomagnification is inconclusive. However, uptake of cadmium from soil by feed crops may result in high levels of cadmium in beef and poultry (especially in the liver and kidneys). And this accumulation of cadmium in the food chain has important implications for human exposure, whether or not significant biomagnification occurs (USPHS 1997).

4. Toxicity

Cadmium has no biochemical or nutritional function, and it is highly toxic to both plants and animals (USPHS 1997, WHO 1992, Alloway 1990). In humans and animals, there is strong evidence that the kidney is the main target organ of cadmium toxicity, following extended exposure (USPHS 1997, Elinder and Jarup 1996, Goyer 1996, Roels *et al.* 1993, Iwata *et al.* 1993, WHO 1992, Mueller *et al.* 1992). Renal damage includes tubular proteinuria (the excretion of low molecular weight proteins) and a decrease in the glomerular filtration rate. The latter results in a depressed re-sorption of enzymes, amino acids, glucose, calcium, copper, and inorganic phosphate. Furthermore, studies have shown that even when cadmium exposure ceases, proteinuria does not decrease, and renal tubular dysfunction and reduced glomerular filtration increase in severity (USPHS 1997, Jarup *et al.* 1997, Elinder and Jarup 1996, Goyer 1996, Iwata *et al.* 1993, WHO 1992, Nriagu 1988).

Other toxic effects of cadmium, based on findings from occupation, animal, and epidemiological studies, can be summarised as follows:

Case studies indicate that calcium deficiency, osteoporosis, or osteomalacia (softening of the bones) can develop in some workers after long-term occupational exposure to high levels of cadmium. A progressive disturbance in the renal metabolism of vitamin D and an increased urinary excretion of calcium is often seen, suggesting that bone changes may be secondary to disruption in kidney vitamin D and calcium metabolism (USPHS 1997, Goyer *et al.* 1994, WHO 1992). In the Jinzu River Basin, a cadmium-contaminated area in Japan, a cadmium induced skeletal disorder known as Itai-Itai disease disabled many children born to women of middle age and poor nutrition (Alloway 1996).

The inhalation of high levels of cadmium oxide fumes or dust is intensely irritating to respiratory tissue, and acute high-level exposures can be fatal. Typical non-fatal symptoms can include severe tracheobronchitis, pneumonitis, and pulmonary oedema, which can develop within hours of exposure (USPHS 1997, Goyer 1996, WHO 1992). At lower levels, lung inflammation have been known to cause emphysema (swelling of the lung air sacs resulting in breathlessness) and dyspnoea (difficult and laboured breathing) (USPHS 1997, Goyer 1996, WHO 1992). Animal studies have confirmed that inhalation exposure to cadmium leads to respiratory injury (USPHS 1997, WHO 1992).

There have been a number of epidemiological studies intended to determine a relationship between occupational (respiratory) exposure to cadmium and lung and prostatic cancer, and these along with animal studies have provided considerable support for the carcinogenic potential of cadmium (IARC 1998, Goyer 1996). Cadmium and certain cadmium compounds are therefore listed by the International Agency for Research on Cancer (IARC) as carcinogenic (IARC 1998). The US Department of Health and Human Services in its 8th Report on Carcinogens, lists cadmium and certain cadmium compounds as Reasonably Anticipated to be Human Carcinogens (USPHS 1998).

In addition to these toxic effects, it has also been suggested that cadmium may play a role in the development of hypertension (high blood pressure) and heart disease (USPHS 1997, Goyer 1996, Elinder and Jarup 1996). It is also known that severe oral exposure can result

in severe irritation to the gastrointestinal epithelium, nausea, vomiting, salivation, abdominal pain, cramps and diarrhoea (USPHS 1997).

Regarding plant toxicity, adverse effects on plant growth and yield have been reported. Alloway (1990) reported stunted growth and toxic signs on leaves of lettuce, cabbage, carrot and radish plants, (which resulted from a cadmium content of around 20 mg/kg in the upper parts of the plants). Other studies have shown reductions in the rates of photosynthesis and transpiration (WHO 1992).

Regarding the toxicity of cadmium to aquatic organisms, numerous findings have been reported. For example, some species of phytoplankton are very sensitive to cadmium, with inhibition of growth observed at concentrations as low as 1 ug/l (Bryan and Langston 1992). Deleterious effects have also been reported in limpets, where correlations between increased levels of cadmium and reduced ability to utilise glucose were found. Reductions in reproduction rates and population numbers in copepods and isopods have been shown at concentrations as low as 5 ug/l,; and exposure to similar levels has resulted in changes in immune function in some fish, and depressed growth seen in juvenile fish and invertebrates (Bryan and Langston 1992, Thuvander 1989). Furthermore the toxicity of low sediment-cadmium concentrations has also been suggested following observations in San Francisco Bay. Here the condition of certain species of clam declined as cadmium concentrations rose from 0.1 to 0.4 mg/kg (Bryan and Langston 1992).

5. Legislation

European Directives and Decisions on water quality and permissible discharges treat cadmium as a priority pollutant. Therefore legislation is concerned with the elimination of pollution caused by cadmium, and not just the reduction. Examples include:

Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more than 1 ug/l of cadmium must be subjected to intensive physical and chemical treatment prior to use.

Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Cadmium is included in List I, and as such water pollution caused by its presence should be eliminated.

Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A maximum permissible concentration of 1 ug/l is set.

Other drinking legislation includes that devised by the Bureau of Indian Standards (1995) and the USEPA (USPHS 1997), which both set a maximum permissible concentration for cadmium of 10 ug/l, although the USEPA does have plans to reduce this limit to 5 ug/l. The WHO currently recommends a guideline level of 5 ug/l (WHO 1993).

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-1 mg/kg as being typical of uncontamination. Anything above this is classifies as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations

for cadmium range from 8-30 mg/kg. However resulting soil concentrations must not exceed 3 mg/kg (EC, UK, France, Germany) (Alloway 1990).

Finally, cadmium is included in the list of priority hazardous substances agreed by the Third North Sea Conference (MINDEC 1990), Annex 1A to the Hague Declaration, and confirmed at the Fourth Conference in Esjberg, Denmark, in 1995 (MINDEC 1995). Here it was agreed that environmental concentrations of hazardous substances should be reduced to near background levels within the next 25 years. An objective further reinforced in the Sintra Statement at the 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a). Cadmium has been selected for priority action, and as such as included in Annex 2 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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Manganese (Mn)

Manganese is an essential trace metal, although human and animal exposure to high levels can cause serious illness. Workers chronically exposed to high levels of manganese in the air have suffered both mental and emotional disturbances, along with increased slowness and clumsiness of body movements. This combination of symptoms is a disease called manganism. The symptoms can be reduced by medical treatment, but due to the high levels of manganese accumulated in the brain, any brain injury is often permanent (ATSDR 1997). It is not certain whether eating or drinking elevated levels of manganese can cause manganism or not. In one report, humans exposed to contaminated drinking water, developed symptoms similar to those seen in manganese miners or steel workers, but it is not certain if the effects were caused by the manganese alone. Another report found that people who drank water with above average levels of manganese seemed to have a slightly higher frequency of symptoms such as weakness, stiff muscles, and trembling of the hands. However, these symptoms are not specific for manganese, and might have been caused by other factors (ATSDR 1997).

Studies in animals have shown that very high levels of manganese in food or water can

cause changes in the brain, suggesting that high levels might cause brain injury. In addition, animal studies have indicated that manganese may also be a reproductive toxicant, especially to males, injuring the testes and causing impotence.

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